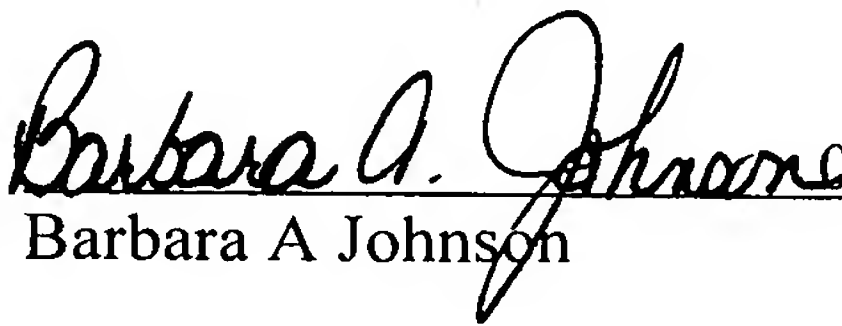


IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appln. No. :	10/580,812)	CERTIFICATE OF MAIL
Applicant :	Keith R. Minnich et al)	I hereby certify that this correspondence
Filed:	05/25/2006)	is being deposited with the United States
Title :	Method for Production of)	Postal Services with sufficient postage
	High Pressure Steam from)	as first class mail in an envelope
	Produced Water)	addressed to: Commissioner for Patents,
)	P.O. Box 1450, Alexandria, VA 22313-
Docket No. :	4553-00025)	1450, on this 27th day of July, 2007.
)	
)	 07/27/2007
)	Barbara A Johnson Date
)	
)	

PETITION UNDER 37 CFR 1.47(A) TO ACCEPT FILING
WHEN INVENTOR REFUSES TO SIGN

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

This Petition is being filed for acceptance of the above-identified patent application under 37 CFR 1.47(a). Enclosed with this Petition are the following:

1. Two Statements of Facts in Support of Filing on Behalf of the Nonsigning Inventors, signed by Ms. Lisa Schollaert and Mr. Robert D. Pietrala, both of whom have first hand knowledge of facts concerning the refusal to sign by three of the four inventors.

2. A Declaration setting forth the full name, address and citizenship of the three non-signing inventors, as well as the full name, address and citizenship of the one signing co-inventor.

08/03/2007 MKAYPAGH 00000073 10580812

03 FC:1464

130.00 OP

3. The Petition fee of \$130.00 (37 CFR 1.17(I)).

Application No. 10/580,812
Applicant: Keith R. Minnich et al
Petition under 37 CFR 1.47(a) to Accept Filing
When Inventor Refuses to Sign Dated July 27, 2007

It is submitted that these Statements of Facts provide the necessary evidence from one having firsthand knowledge of the facts that the application materials including the Declaration were received by the non-signing inventors, and that their silence and lack of cooperation despite repeated attempts to contact them is evidence of their refusal to sign the Declaration.

Based on the foregoing, Petitioner requests that this Petition be granted, so that a filing receipt can be obtained and the application can be advanced to examination.

Respectfully submitted,

ANDRUS, SCEALES, STARKE & SAWALL, LLP

By: 
William L. Falk
Reg. No. 27,709

ATTORNEYS FOR APPLICANT:
Andrus, Scales, Starke & Sawall, LLP
100 East Wisconsin Avenue, Suite 1100
Milwaukee, Wisconsin 53202
Telephone: (414) 271-7590
Facsimile: (414) 271-5770

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appln. No. :	10/580,812)	CERTIFICATE OF MAILING
Applicant :	Keith R. Minnich et al)	I hereby certify that this correspondence
Filed:	05/25/2006)	is being deposited with the United States
Title :	Method for the Production)	Postal Service with sufficient postage as
	of High Pressure Steam)	first class mail in an envelope addressed
	from Produced Water)	to: Commissioner for Patents, P.O. Box
Docket No. :	4553-00025)	1450, Alexandria, VA 22313-1450, on
)	this <u>27th</u> day of <u>July</u> , 2007.
)	<i>Barbara A. Johnson</i> <u>7-27-07</u>
)	Barbara A. Johnson Date
)	
)	
)	

STATEMENT OF FACTS IN SUPPORT OF FILING ON BEHALF
OF NON-SIGNING INVENTORS UNDER 37 C.F.R. §1.47

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

This statement is made as to the facts that are relied upon to establish the diligent effort made to secure the execution of the Declaration by the non-signing inventors, Mr. Keith R. Minnich, Mr. Mark C. Nicholson and Mr. Ramkumar Karlapudi, for the above-identified patent application subsequent to filing thereof in the U.S. Patent and Trademark Office.

This statement is being made by the available person having firsthand knowledge of the facts recited herein. The person making this statement is:

Ms. Lisa Schollaert
Executive Assistant to the CEO
Aquatech International Corporation
1 Four Coins Drive
Canonsburg, PA 15317-1776

Application No. 10/580,812

Applicant: Keith R. Minnich et al

Statement of Facts in Support of Filing on Behalf

of Non-Signing Inventors Under 37 C.F.R. §1.47 Dated 19 July 2007

1. The present invention was filed in the USPTO on May 25, 2006 and received Serial No. 10/580,812. This application is the U.S. national stage application of International Application PCT/US2004/039515 filed November 24, 2004. The International Application claimed priority of U.S. Provisional Application Serial No. 60/525,578 filed November 26, 2003. The four inventors of the '812 application are Keith R. Minnich, Mark C. Nicholson, Ramkumar Karlapudi and Richard M. Schoen.

2. Shortly after filing the PCT International Application, the four inventors were presented an Assignment document which assigned the entire right, title and interest of the invention in the subject '812 application, as well as foreign applications to Aquatech International Corp. All four inventors of the subject '812 application executed the Assignment, a copy of which is attached herewith as Exhibit A. The Assignment was recorded July 21, 2006 at Reel 017976/Frame 450.

3. After entering the national stage in the U.S. by filing the subject '812 application on May 25, 2006, the four inventors were presented with a copy of the subject application as filed along with a copy of the Declaration for execution. One inventor Richard M. Schoen signed the Declaration on May 10, 2007. Attached Exhibit B shows a copy of the signed Declaration. However, the other three inventors Keith R. Minnich, Mark C. Nicholson and Ramkumar Karlapudi left the employ of Aquatech International Corp. and copies of the subject application and the Declaration were sent separately to each of the three inventors as set forth below. A copy of the subject application and Declaration as sent to each inventor is shown in Exhibit C attached hereto.

Application No. 10/580,812

Applicant: Keith R. Minnich et al

Statement of Facts in Support of Filing on Behalf

of Non-Signing Inventors Under 37 C.F.R. §1.47 Dated 19 July 2007

4. On May 9, 2007 a copy of the subject application and the Declaration was send via Fed Ex to Keith R. Minnich at his last known address by my cover letter, a copy of which is attached in Exhibit D. Also attached is Exhibit E which shows that Mr. Minnich refused to accept the Fed Ex delivery on May 14, 2007 and that the package was returned to the shipper as shown by the Fed Ex air bill and tracking details.

5. On May 9, 2007 a copy of the subject application and the Declaration was sent via Fed-ex to Mark C. Nicholson at his last known address by my cover letter, a copy of which is attached in Exhibit F. Also attached is Exhibit G which includes Fed-ex air bill and tracking details and verifies that the enclosures of Exhibit F were delivered on May 10, 2007 and received and signed for by J. Nicholson.

6. On May 9, 2007, a copy of the subject application and the Declaration was sent via Fed Ex to Ramkumar Karlapudi at his last known address by my cover letter, a copy of which is attached in Exhibit H. Also attached is Exhibit I which includes Fed Ex air bill and tracking details and verifies that the enclosures of Exhibit H were delivered on May 10, 2007 and received and signed for by R. Karlapudi.

7. No response has been received from any of the three non-signing inventors Keith R. Minnich, Mark C. Nicholson and Ramkumar Karlapudi.

Application No. 10/580,812

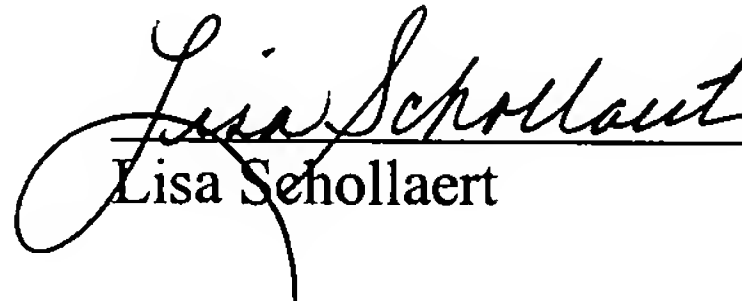
Applicant: Keith R. Minnich et al

Statement of Facts in Support of Filing on Behalf

of Non-Signing Inventors Under 37 C.F.R. §1.47 Dated 19 July 2007

8. The above facts clearly demonstrate that despite being presented with the subject application and the Declaration therefore, Mr. Minnich, Mr. Nicholson and Mr. Karlapudi have refused to sign the Declaration. Accordingly, the above facts demonstrate a bonafide and diligent effort was made to obtain signatures of these three non-signing inventors to no avail.

Dated: July 19, 2007


Lisa Schollaert

ATTORNEYS FOR APPLICANT:

Andrus, Sceales, Starke & Sawall, LLP

100 East Wisconsin Avenue, Suite 1100

Milwaukee, Wisconsin 53202

Telephone: (414) 271-7590

Facsimile: (414) 271-5770

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appln. No. :	10/580,812)	CERTIFICATE OF MAILING
Applicant :	Keith R. Minnich et al)	I hereby certify that this correspondence
Filed:	05/25/2006)	is being deposited with the United States
Title :	Method for the Production)	Postal Service with sufficient postage as
	of High Pressure Steam)	first class mail in an envelope addressed
	from Produced Water)	to: Commissioner for Patents, P.O. Box
Docket No. :	4553-00025)	1450, Alexandria, VA 22313-1450, on
)	this <u>27th</u> day of <u>July</u> , 2007.
)	<u>Barbara A. Johnson</u> <u>7-27-07</u>
)	Barbara A. Johnson Date
)	
)	
)	

**SUPPLEMENTAL STATEMENT OF FACTS IN SUPPORT OF FILING ON
BEHALF OF NON-SIGNING INVENTORS UNDER 37 C.F.R. §1.47**

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

This statement is made as to the facts that are relied upon to establish the diligent effort made to secure the execution of the Declaration by the non-signing inventors, Mr. Keith R. Minnich and Mr. Mark C. Nicholson, for the above-identified patent application subsequent to filing thereof in the U.S. Patent and Trademark Office.

This statement is being made by the available person having firsthand knowledge of the facts recited herein. The person making this statement is:

Mr. Robert D. Pietrala
Vice President and General Counsel
Aquatech International Corporation
1 Four Coins Drive
Canonsburg, PA 15317-1776

Application No. 10/580,812

Applicant: Keith R. Minnich et al

Statement of Facts in Support of Filing on Behalf

of Non-Signing Inventors Under 37 C.F.R. §1.47 Dated July 25, 2007

1. Attempts to obtain signatures on the Declaration of the subject application from the non-signing inventors, Keith R. Minnich and Mark C. Nicholson, have been documented by Lisa Schollaert in a Statement of Facts in Support of Filing on Behalf of the Non-Signing Inventors under 37 CFR §1.47 separately appended hereto.

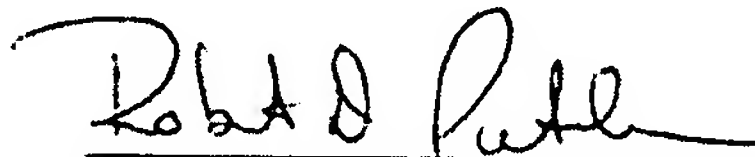
2. Pursuant to a request from the attorneys representing Keith R. Minnich and Mark C. Nicholson, a further attempt to obtain the Declaration signatures of these non-signing inventors was made.

3. On July 3, 2007, I sent via Fed Ex a cover letter of instruction along with a complete copy of the subject application as filed along with the Declaration. Attached is Exhibit J which includes a copy of my July 3, 2007 cover letter to Ms. Danielle L. Hodnicki, attorney for the non-signing inventors, the complete copy of the application and the Declaration. Also attached is Exhibit K which includes the Fed Ex air bill and tracking details, and verifies that the enclosures of Exhibit J were received and signed for by D. Santoro of the Tucker, Arensberg firm on July 5, 2007.

4. To date, no response whatsoever has been received from Ms. Hodnicki or the non-signing inventors.

The above facts further demonstrate that despite being presented again with the subject application and the Declaration, Mr. Minnich and Mr. Nicholson refused to sign the Declaration by acquiescence. Accordingly, the above facts further demonstrate a bona fide and diligent effort was made to obtain the signatures of Mr. Minnich and Mr. Nicholson on the Declaration, but to no avail.

Dated: July 25, 2007


Robert D. Pietrala

Type a plus sign (+) inside this box [+]

Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION		Attorney Docket Number 4553-00025
		First Named Inventor Keith R. Minnich et al
COMPLETE IF KNOWN		
		Application Number 10/580,812
		Filing Date
		Group Art Unit
		Examiner Name

Declaration ☐ Submitted with Initial Filing Declaration ☒ Submitted after Initial Filing

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Method for Production of High Pressure Steam from Produced Water

(Title of the Invention)

the specification of which ☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY) 11/24/2004 as United States Application Number or PCT

International Number (if applicable) PCT/US2004/039515 and was amended on (MM/DD/YYYY)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under Title 35, United States Code §119(a)-(d) or §365(b) of any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or §365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent, inventor's or breeder's rights certificate(s), or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Copy Attached?	
				YES	NO
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

☐ Additional foreign application numbers are listed on a supplemental priority sheet attached hereto:

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)	Additional provisional Application numbers are listed on a supplemental priority sheet attached hereto.
60/525,578	11/26/2003	

Type a plus sign (+) inside this box [+]

Attorney Docket Number	4553-00025
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DECLARATION

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §365© of any PCT international application designated the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States of PCT International application in the manner provided by the first paragraph of Title 35, United States Code §112. I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)

☐ Additional U.S. or PCT international application numbers are listed on a supplemental priority sheet attached hereto.

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

☒ Customer Number: **26753**

Name	Registration Number	Name	Registration Number
Daniel D. Fetterley	20,323	Edward R. Williams, Jr.	36,057
George H. Solveson	25,927	Aaron T. Olejniczak	54,853
Gary A. Essmann	29,376	Peter T. Holsen	54,180
Thomas M. Wozny	28,922	Christopher M. Scherer	50,655
Michael E. Taken	28,120	M. Scott McBride	52,008
Joseph J. Jochman, Jr.	25,058	Benjamin R. Imhoff	60,036
Joseph D. Kuborn	40,689	William L. Falk	27,709

☐ Additional attorney(s) and/or agent(s) named on a supplemental sheet attached hereto.

Direct all correspondence to: ☒ Customer Number: **26753** OR ☒ Correspondence address below

NAME	Thomas M. Wozny				
	ANDRUS, SCEALES, STARKE & SAWALL, LLP				
ADDRESS	100 East Wisconsin Avenue				
	Suite 1100				
CITY	Milwaukee	STATE	Wisconsin	ZIP CODE	53202-4178
COUNTRY	U.S.A.	TELEPHONE	(414) 271-7590	FAX	(414) 271-5770

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor: ☐ A petition has been filed for this unsigned inventor

Given Name (first and middle [if any]) Keith R.	Family Name or Surname Minnich
Inventor's Signature	Date

Residence: City Pewaukee	State WI	Country US	Citizenship United States
------------------------------------	--------------------	----------------------	-------------------------------------

Mailing Address W291 N3821 Round Hill Circle			
City Pewaukee	State WI	Zip 53072	Country US

☒ Additional inventors are being named on supplemental sheet(s) attached hereto.


Please type a plus sign (+) inside this box [+]

Attorney Docket Number	4553-00025
------------------------	------------

DECLARATION	ADDITIONAL INVENTOR(S) Supplemental Sheet
-------------	--

Name of Additional Joint Inventor, if any:		<input type="checkbox"/> A petition has been filed for this unsigned inventor	
Given Name (first and middle [if any]) Mark C.		Family Name or Surname Nicholson	
Inventor's Signature		Date	
Residence: City Pewaukee	State WI	Country US	Citizenship United States
Mailing Address W269 N2740 Lelah Avenue			
City Pewaukee	State WI	Zip 53072	Country US

Name of Additional Joint Inventor, if any:		<input type="checkbox"/> A petition has been filed for this unsigned inventor	
Given Name (first and middle [if any]) RamKumar		Family Name or Surname Karlapudi	
Inventor's Signature		Date	
Residence: City Lake Mary	State FL	Country US	Citizenship India
Mailing Address 1705 Cherry Ridge Drive			
City Lake Mary	State FL	Zip 32746	Country US

Name of Additional Joint Inventor, if any:		<input type="checkbox"/> A petition has been filed for this unsigned inventor	
Given Name (first and middle [if any]) Richard M.		Family Name or Surname Schoen	
Inventor's Signature 		Date 5/10/07	
Residence: City Hartland	State WI	Country US	Citizenship United States
Mailing Address N67 W29767 Hartling Road			
City Hartland	State WI	Zip 53029	Country US

☐ Additional inventors are being named on supplemental sheet(s) attached hereto.

ASSIGNMENT

ASSIGNMENT made by **Keith R. Minnich**, of W291 N3821 Round Hill Circle, Pewaukee, Wisconsin 53072, U.S.A., a United States citizen, and **Mark C. Nicholson**, of W269 N2740 Lelah Avenue, Pewaukee, Wisconsin 53072, U.S.A., a United States citizen, **RamKumar Karlapudi** of 1981 Fox Croft Lane, Waukesha, Wisconsin 53189, U.S.A., an Indian citizen, and **Richard M. Schoen** of N67 W29767 Hartling Road, Hartland, Wisconsin 53029, U.S.A., a United States citizen, to **Aquatech International Corporation**, a corporation organized under the laws of the State of Pennsylvania, and located and doing business at One Four Coins Drive, Canonsburg, Pennsylvania 15317, U.S.A.

IN CONSIDERATION of One Dollar (\$1.00) and other good and valuable considerations, the receipt of which is hereby acknowledged, said **Keith R. Minich**, **Mark C. Nicholson**, **RamKumar Karlapudi**, and **Richard M. Schoen** hereby sell, assign and transfer to said **Aquatech International Corporation**, its successors and assigns, the entire right, title and interest in:

METHOD FOR PRODUCTION OF HIGH PRESSURE STEAM FROM PRODUCED WATER

and the invention therein as set forth in their application for United States Letters Patent therefor, and in and to said application and any divisions or continuations thereof, and any Letters Patent obtained for the said invention in the United States and foreign countries, or issuing out of said application or any such division or continuation thereof, and any reissues, reexamination or extension of any such Letters Patent.

The Commissioner of Patents is hereby authorized and requested to issue Letters Patent for said invention to said **Aquatech International Corporation**, as assignee of the entire right, title and interest therein.

Customer Number: 26753



And, said **Keith R. Minich, Mark C. Nicholson, RamKumar Karlapudi, and Richard M. Schoen** hereby covenant that they have full right to convey the entire right, title and interest in said invention, and that they have not executed and will not execute any agreement in conflict herewith.

And they further covenant that they will, at any time, upon request, execute and deliver any and all papers that may be necessary or desirable to perfect the title in said **Aquatech International Corporation**, to said invention or any Letters Patent that may be granted therefor, and if said **Aquatech International Corporation**, or its assignee, desire to make a substitute, divisional or continuation application for said invention, or to secure a reissue, reexamination or extension of said Letters Patent, to file a disclaimer relating thereto, or an application for a corresponding patent in any foreign country, that they will upon request, sign all papers, make all rightful oaths, and do all lawful acts requisite for the said purposes, but at the expense of said **Aquatech International Corporation**.

Keith R. Minich, Mark C. Nicholson, RamKumar Karlapudi, and Richard M. Schoen further hereby acknowledge that the entire beneficial interest in the invention to which the above application relates is irrevocably vested in the assignee including the right to make application for protection in all countries abroad and to claim priority under the International Convention for such applications and hereby assent to the making of any such applications, with or without priority claim, and of any divisional application resulting therefrom.

And, they further covenant that they will at all times communicate to the said **Aquatech International Corporation**, its successors, assigns or legal representatives, all facts relating to said invention and Letters Patent, or the history thereof, known to them, and testify as the same in interferences or other litigation, when requested so to do.

We hereby authorize the above-mentioned assignee or the attorney of record to insert in this instrument the filing date and serial number of our said application:

Serial Number: 10/580,812

Filing Date: May 25, 2006

Executed and delivered this 17 day of January, ~~2004~~ ²⁰⁰⁵.

Inventor *Keith R. Minnich*
Keith R. Minnich

State of Wisconsin)

County of Waukesha)

Personally appeared before me this 17 day of January, ~~2004~~ ²⁰⁰⁵, **Keith R. Minnich**, to me known to be the person whose name is subscribed to the foregoing instrument, and acknowledged that he signed, sealed and delivered the said instrument as his free and voluntary act and deed for the uses and purposes therein set forth.

[Signature]
Notary Public
My Commission expires June 26, 2005

(SEAL)

Executed and delivered this 17 day of January, ~~2004~~ ²⁰⁰⁵.

Inventor *Mark C. Nicholson*
Mark C. Nicholson

State of Wisconsin)

County of Waukesha)

Personally appeared before me this 17 day of January, ~~2004~~ ²⁰⁰⁵, **Mark C. Nicholson**, to me known to be the person whose name is subscribed to the foregoing instrument, and acknowledged that he signed, sealed and delivered the said instrument as his free and voluntary act and deed for the uses and purposes therein set forth.

[Signature]
Notary Public
My Commission expires June 26, 2005

(SEAL)

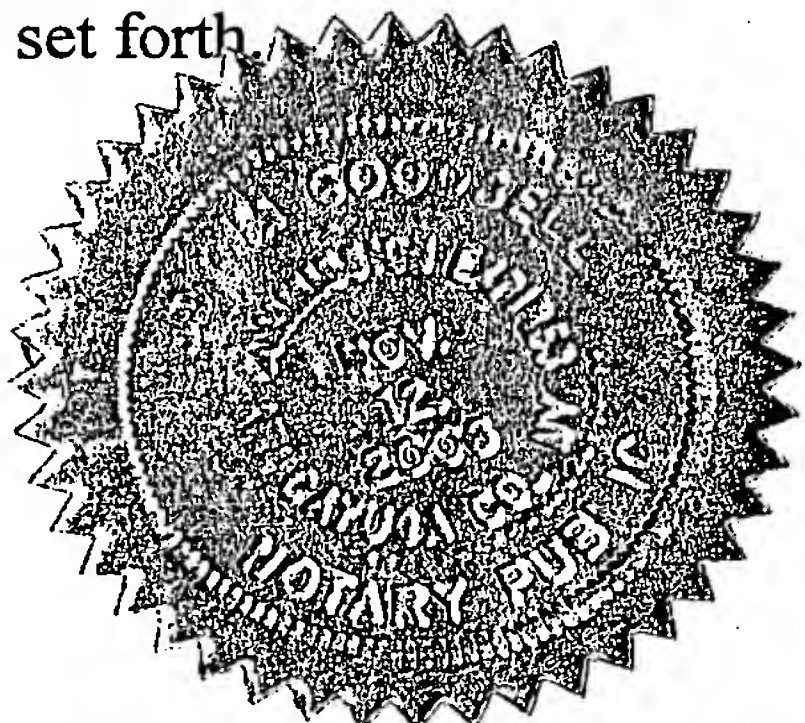
Customer Number: 26753

Executed and delivered this 04 day of January, 2004.5 *mg*

Inventor *Ram*
RamKumar Karlapudi

State of New York)
County of Cortland)

mg Personally appeared before me this 04 day of January, 2004.5 **RamKumar Karlapudi**, to me known to be the person whose name is subscribed to the foregoing instrument, and acknowledged that he signed, sealed and delivered the said instrument as his free and voluntary act and deed for the uses and purposes therein set forth.



Judy M. Goodsell
Notary Public
My Commission Nov. 12, 2006

Executed and delivered this 04 day of January, 2004.5

Inventor *Richard M. Schoen*
Richard M. Schoen

State of Wisconsin)
County of Waukesha)

Personally appeared before me this 17 day of January, 2005, ~~2004~~, **Richard M. Schoen**, to me known to be the person whose name is subscribed to the foregoing instrument, and acknowledged that he signed, sealed and delivered the said instrument as his free and voluntary act and deed for the uses and purposes therein set forth.

(SEAL)

[Signature]
Notary Public
My Commission Expires June 26, 2005

Customer Number: 26753

Type a plus sign (+) inside this box [+]

Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION		Attorney Docket Number 4553-00025
		First Named Inventor Keith R. Minnich et al
COMPLETE IF KNOWN		
		Application Number 10/580,812
		Filing Date
		Group Art Unit
		Examiner Name

Declaration ☐ Submitted with Initial Filing Declaration ☒ Submitted after Initial Filing

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Method for Production of High Pressure Steam from Produced Water

(Title of the Invention)

the specification of which ☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY) 11/24/2004 as United States Application Number or PCT

International Number (if applicable) PCT/US2004/039515 and was amended on (MM/DD/YYYY)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

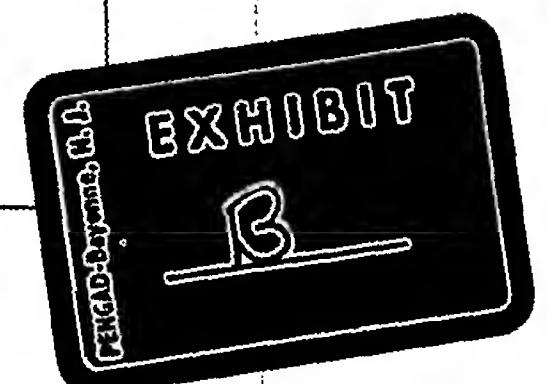
I hereby claim foreign priority benefits under Title 35, United States Code §119(a)-(d) or §365(b) of any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or §365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent, inventor's or breeder's rights certificate(s), or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Copy Attached?	
				YES	NO
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

☐ Additional foreign application numbers are listed on a supplemental priority sheet attached hereto:

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)	Additional provisional <input type="checkbox"/> Application numbers are listed on a supplemental priority sheet attached hereto.
60/525,578	11/26/2003	



Type a plus sign (+) inside this box [+]

Attorney Docket Number	4553-00025
------------------------	------------

DECLARATION

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §365© of any PCT international application designated the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States of PCT International application in the manner provided by the first paragraph of Title 35, United States Code §112. I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)

☐ Additional U.S. or PCT international application numbers are listed on a supplemental priority sheet attached hereto.

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

☒ Customer Number: **26753**

Name	Registration Number	Name	Registration Number
Daniel D. Fetterley	20,323	Edward R. Williams, Jr.	36,057
George H. Solveson	25,927	Aaron T. Olejniczak	54,853
Gary A. Essmann	29,376	Peter T. Holsen	54,180
Thomas M. Wozny	28,922	Christopher M. Scherer	50,655
Michael E. Taken	28,120	M. Scott McBride	52,008
Joseph J. Jochman, Jr.	25,058	Benjamin R. Imhoff	60,036
Joseph D. Kuborn	40,689	William L. Falk	27,709

☐ Additional attorney(s) and/or agent(s) named on a supplemental sheet attached hereto.

Direct all correspondence to: ☒ Customer Number: **26753** OR ☒ Correspondence address below

NAME	Thomas M. Wozny				
	ANDRUS, SCEALES, STARKE & SAWALL, LLP				
ADDRESS	100 East Wisconsin Avenue				
	Suite 1100				
CITY	Milwaukee	STATE	Wisconsin	ZIP CODE	53202-4178
COUNTRY	U.S.A.	TELEPHONE	(414) 271-7590	FAX	(414) 271-5770

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor: ☐ A petition has been filed for this unsigned inventor

Given Name (first and middle [if any]) Keith R.	Family Name or Surname Minnich
Inventor's Signature	Date

Residence: City Pewaukee	State WI	Country US	Citizenship United States
------------------------------------	--------------------	----------------------	-------------------------------------

Mailing Address W291 N3821 Round Hill Circle			
City Pewaukee	State WI	Zip 53072	Country US

☒ Additional inventors are being named on supplemental sheet(s) attached hereto.

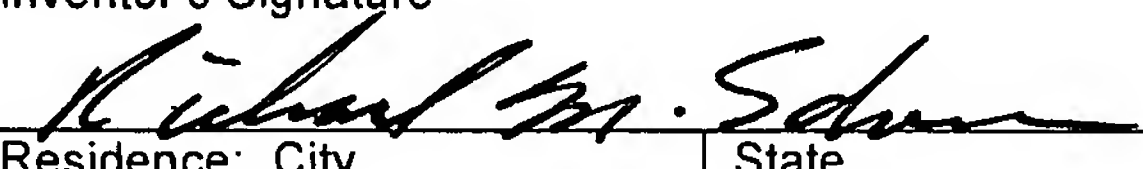
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Attorney Docket Number	4553-00025
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DECLARATION	ADDITIONAL INVENTOR(S) Supplemental Sheet
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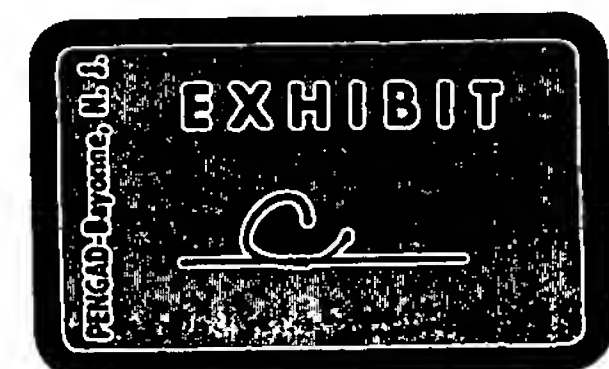
Name of Additional Joint Inventor, if any:		<input type="checkbox"/> A petition has been filed for this unsigned inventor	
Given Name (first and middle [if any]) Mark C.		Family Name or Surname Nicholson	
Inventor's Signature		Date	
Residence: City Pewaukee	State WI	Country US	Citizenship United States
Mailing Address W269 N2740 Lelah Avenue			
City Pewaukee	State WI	Zip 53072	Country US

Name of Additional Joint Inventor, if any:		<input type="checkbox"/> A petition has been filed for this unsigned inventor	
Given Name (first and middle [if any]) RamKumar		Family Name or Surname Karlapudi	
Inventor's Signature		Date	
Residence: City Lake Mary	State FL	Country US	Citizenship India
Mailing Address 1705 Cherry Ridge Drive			
City Lake Mary	State FL	Zip 32746	Country US

Name of Additional Joint Inventor, if any:		<input type="checkbox"/> A petition has been filed for this unsigned inventor	
Given Name (first and middle [if any]) Richard M.		Family Name or Surname Schoen	
Inventor's Signature 		Date 5/10/07	
Residence: City Hartland	State WI	Country US	Citizenship United States
Mailing Address N67 W29767 Hartling Road			
City Hartland	State WI	Zip 53029	Country US

☐ Additional inventors are being named on supplemental sheet(s) attached hereto.

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A SUBMISSION UNDER 35 U.S.C. 371		ATTORNEY'S DOCKET NUMBER 4553-00025
INTERNATIONAL APPLICATION NO. PCT/US2004/039515	INTERNATIONAL FILING DATE 24 November 2004	PRIORITY DATE CLAIMED 26 November 2003
TITLE OF INVENTION Method for Production of High Pressure Steam from Produced Water		
APPLICANT(S) FOR DO/EO/US Keith R. Minnich, Mark C. Nicholson, RamKumar Karlapudi, Richard M. Schoen		
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:		
1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a submission under 35 U.S.C. 371.		
2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a submission under 35 U.S.C. 371.		
3. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.		
4. <input checked="" type="checkbox"/> The US has been elected (Article 31).		
5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ul style="list-style-type: none"> a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> has been communicated by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 		
6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). <ul style="list-style-type: none"> a. <input checked="" type="checkbox"/> is attached hereto. b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). 		
7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ul style="list-style-type: none"> a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 		
8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).		
9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).		
10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).		
Items 11 to 20 below concern document(s) or information included:		
11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.		
12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.		
13. <input checked="" type="checkbox"/> A preliminary amendment.		
14. <input type="checkbox"/> An Application Data Sheet under 37 CFR 1.76.		
15. <input type="checkbox"/> A substitute specification.		
16. <input type="checkbox"/> A power of attorney and/or change of address letter.		
17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 37 CFR 1.821- 1.825.		
18. <input type="checkbox"/> A second copy of the published International Application under 35 U.S.C. 154(d)(4).		
19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).		



Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO. PCT/US2004/039515	ATTORNEY'S DOCKET NUMBER 4553-00025
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20. Other items or information:

 A) Small Entity Status

The following fees have been submitted				CALCULATIONS	PTO USE ONLY
21.	<input checked="" type="checkbox"/>	Basic national fee (37 CFR 1.492(a)).....	\$300	\$ 300.00	
22.	<input checked="" type="checkbox"/>	Examination fee (37 CFR 1.492(c))		\$ 200.00	
If the written opinion prepared by ISA/US or the international preliminary examination report prepared by IPEA/US indicates all claims satisfy provisions of PCT Article 33(1)-(4).....				\$ 0	
All other situations.....				\$200	
23.	<input checked="" type="checkbox"/>	Search fee (37 CFR 1.492(b))		\$ 400.00	
If the written opinion of the ISA/US or the International preliminary examination report prepared by IPEA/US indicates all claims satisfy provisions of PCT Article 33(1)-(4).....				\$ 0	
Search fee (37 CFR 1.445(a)(2)) has been paid on the international application to the USPTO as an International Searching Authority.....				\$100	
International Search Report prepared by an ISA other than the US and provided to the Office or previously communicated to the US by the IB.....				\$400	
All other situations.....				\$500	
TOTAL OF 21, 22 and 23 =				900.00	
<input type="checkbox"/> Additional fee for specification and drawings filed in paper over 100 sheets (excluding sequence listing in compliance with 37 CFR 1.821(c) or (e) or computer program listing in an electronic medium) (37 CFR 1.492(j)). The fee is \$250 for each additional 50 sheets of paper or fraction thereof.					
Total Sheets	Extra Sheets	Number of each additional 50 or fraction thereof (round up to a whole number)	RATE		
- 100 =	/50 =		x \$250.00	\$ 0.00	
Surcharge of \$130.00 for furnishing any of the search fee, examination fee, or the oath or declaration after the date of commencement of the national stage (37 CFR 1.492(h)).				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$ 900.00	
Total claims	34 - 20 =	14	x \$50.00	\$ 700.00	
Independent claims	1 - 3 =	0	x \$200.00	\$ 0.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$360.00	\$ 0.00	
TOTAL OF ABOVE CALCULATIONS =				\$ 1,600.00	
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. Fees above are reduced by 1/2.				800.00	
SUBTOTAL =				\$ 800.00	
Processing fee of \$130.00 for furnishing the English translation later than 30 months from the earliest claimed priority date (37 CFR 1.492(i)).				\$	
TOTAL NATIONAL FEE =				\$ 800.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				\$	
TOTAL FEES ENCLOSED =				\$ 800.00	
				Amount to be refunded:	\$
				Amount to be charged	\$

- a. ☒ A check in the amount of \$ 800.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. 01.2000 in the amount of \$ _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 01.2000. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the International Application to pending status.

SEND ALL CORRESPONDENCE TO:

Andrus, Sceales, Starke & Sawall, LLP, 100 East Wisconsin Avenue, Suite 1100, Milwaukee, WI 53202-4178, (414) 271-7590, Facsimile: (414) 271-5770

CERTIFICATE OF EXPRESS MAIL: I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as EXPRESS MAIL-POST OFFICE TO ADDRESSEE, in an envelope addressed to: BOX PCT COMMISSIONER OF PATENTS, P.O. Box 1450, Alexandria, VA 22313-1450 on May 25, 2006

The Express Mail Label is EV415015400US

Dorothy A. Hauser May 25, 2006
Dorothy A. Hauser Date

Thomas M. Wozny
SIGNATURE

Thomas M. Wozny
NAME

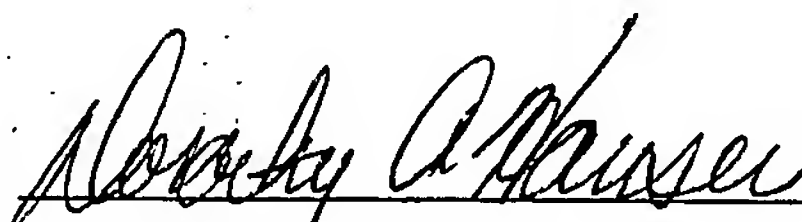
28,922

REGISTRATION NUMBER

EV415015400US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of:)	CERTIFICATE OF EXPRESS MAILING
Keith R. Minnich)	I hereby certify that this correspondence is
Mark C. Nicholson)	being deposited with the United States
RamKumar Karlapudi)	Postal Service with sufficient postage as
Richard M. Schoen)	EXPRESS MAIL in an envelope addressed
)	to: Commissioner for Patents, Alexandria,
Filed Herein)	VA 22313-1450 on this 25th day of May,
)	2006. The Express Mail Label is
International Appl. No.)	EV415015400US.
PCT/US2004/039515)	
International Filing Date:)	
24 November 2004)	
Priority Date Claimed:)	
26 November 2003)	
Method for Production of High Pressure)	
Steam from Produced Water)	
)	
Attorney Docket No. 4553-00025)	

 May 25, 2006
Dorothy A. Hauser Date

SUPPLEMENT TO TRANSMITTAL LETTER

Mail Stop: PCT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

This application is being filed to enter the national stage of the PCT pursuant to 37 C.F.R. §1.495(c). The application includes the specification, at least one claim, and the filing fee. The Declaration is not included. The inventors are:

- 1) Keith R. Minnich
W291 N3821 Round Hill Circle
Pewaukee, Wisconsin 53072
Citizenship: United States
- 2) Mark C. Nicholson
W269 N2740 Lelah Avenue
Pewaukee, Wisconsin 53072
Citizenship: United States

- 3) RamKumar Karlapudi
1981 Fox Croft Lane
Waukesha, Wisconsin 53189
Citizenship: India
- 4) Richard M. Schoen
N67 W29767 Hartling Road
Hartland, Wisconsin 53029
Citizenship: United States

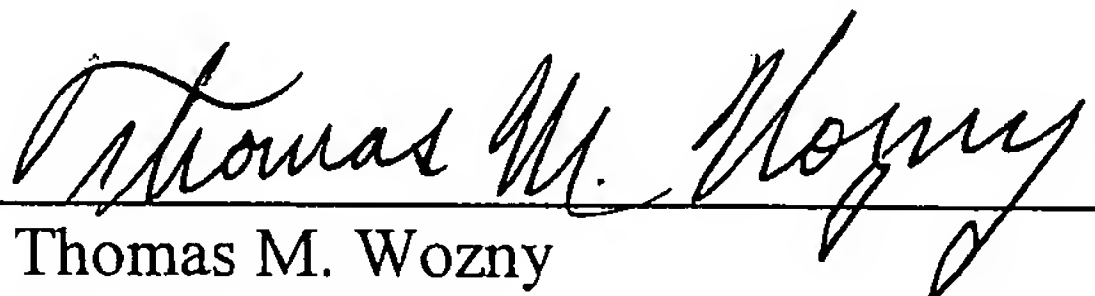
The Declaration will be forwarded promptly upon notification from the U.S. Patent and Trademark Office.

Please address all correspondence and telephone calls regarding this matter to:

Thomas M. Wozny
ANDRUS, SCEALES, STARKE & SAWALL, LLP
100 East Wisconsin Avenue, Suite 1100
Milwaukee, Wisconsin 53202
(414) 271-7590

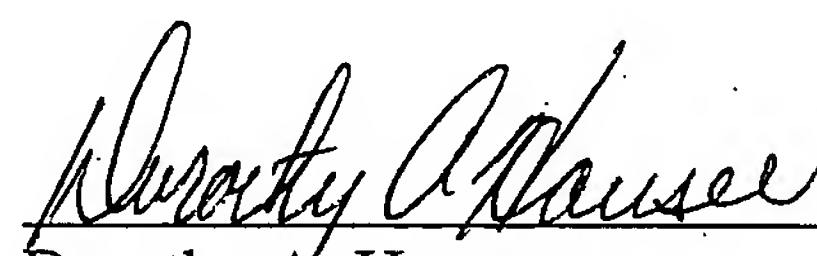
Respectfully submitted,

ANDRUS, SCEALES, STARKE & SAWALL, LLP

By 
Thomas M. Wozny
Reg. No. 28,922

Andrus, Sceales, Starke & Sawall, LLP
100 East Wisconsin Avenue, Suite 1100
Milwaukee, WI 53202
(414) 271-7590

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of:) CERTIFICATE OF EXPRESS MAILING
Keith R. Minnich) I hereby certify that this correspondence is
Mark C. Nicholson) being deposited with the United States
RamKumar Karlapudi) Postal Service with sufficient postage as
Richard M. Schoen) EXPRESS MAIL in an envelope addressed
) to: Commissioner for Patents, Alexandria,
Filed Herein) VA 22313-1450 on this 25th day of May,
) 2006. The Express Mail Label is
International Appl. No.) EV415015400US.
PCT/US2004/039515)
International Filing Date:)
24 November 2004)  May 25, 2006
Priority Date Claimed:) Dorothy A. Hauser Date
26 November 2003)
Method for Production of High Pressure)
Steam from Produced Water)
)
Attorney Docket No. 4553-00025)

PRELIMINARY AMENDMENT

Mail Stop: PCT
 Commissioner for Patents
 P.O. Box 1450
 Alexandria, VA 22313-1450

Sir:

In the matter of the above-identified patent application, please enter the following:

Amendments to the Specification begin on page 2 of this paper.

There are no Amendments to the Claims made in this paper, however, a listing of the claims begins on page 3 of this paper.

There are no Amendments to the Drawings made in this paper.

Remarks begin on page 7 of this paper.

In the Specification:

Please add the following heading and paragraph at page 1, between the title and the first line of text as follows:

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is the U.S. national stage application of International Application PCT/US2004/039515, filed 24 November 2004, which international application was published on June 16, 2005, as International Publication No. WO 2005/054746 in the English language. The International Application claims priority of United States Provisional Application No 60/525,578 filed on 26 November 2003.

Please add the enclosed "Abstract of the Disclosure" as new page 38 to the specification.

In the Claims:

1. (Original) A process for generating steam for downhole injection in a steam flood process for oil recovery, said process comprising:
 - (a) heating a de-oiled produced water stream containing water, dissolved solutes, and dissolved gases, said dissolved solutes further comprising at least one molecular species which is at low ionization levels when in solution at around neutral pH,
 - (b) raising the pH of said heated, produced water stream to maintain the solubility of said molecular species therein at a selected concentration factor,
 - (c) pressurizing and directing said produced water stream to a circulating concentrated brine in a produced water evaporator, said evaporator having a plurality of heat transfer surfaces,
 - (d) distributing said circulating brine across a first surface of at least one of said plurality of heat transfer surfaces to generate a steam vapor suitable for injection into a selected geological formation to fluidize oil,
 - (e) discharging at least some of said brine as an evaporator blowdown stream,
 - (f) distributing steam from a watertube boiler across a second surface of at least one of said plurality of heat transfer surfaces to condense said steam as a condensate,
 - (g) returning said condensate to said watertube boiler for steam production, and,
 - (h) discharging at least some of said condensate as a boiler blowdown to the produced water evaporator.
2. (Original) The process as set forth in claim 1, wherein said dissolved solutes further comprise hardness cations in a quantity that produces a scale deposition on said first surface of said heat transfer surfaces at said selected concentration factor.
3. (Original) The process as set forth in claim 1, wherein said produced water stream further comprises at least some non-hydroxide alkalinity.

4. (Original) The process as set forth in claim 1, wherein the pH is raised to between 10 and 11 and maintained in said evaporator circulating brine.
5. (Original) The process as set forth in claim 1, wherein the pH is raised to between 11 and 12 and maintained in said evaporator circulating brine.
6. (Original) The process as set forth in claim 1, wherein the pH is raised to between 12 and 13 and maintained in said evaporator circulating brine.
7. (Original) The process as set forth in claim 1, wherein the pH is raised to greater than or at least about 13 and maintained in said evaporator circulating brine.
8. (Original) The process according to claim 1, wherein the step of raising the pH is accomplished by addition of an inorganic base in aqueous solution, said base selected from the group consisting of sodium hydroxide, and potassium hydroxide.
9. (Original) The process as set forth in claim 3, wherein a portion or substantially all non-hydroxide alkalinity in said produced water stream is removed.
10. (Original) The process as set forth in claim 9, wherein the step of removing said non-hydroxide alkalinity, is further comprised of lowering the pH of said produced water stream to release at least some free carbon dioxide.
11. (Original) The process as set forth in claim 10, wherein the step of adjusting pH is accomplished by the addition of hydrochloric acid or sulfuric acid.
12. (Original) The process according to claim 1, wherein said produced water evaporator comprises a falling thin film evaporator, operating as a single unit, or operating in parallel, to generate said steam and said blowdown stream.
13. (Original) The process according to claim 1, wherein said produced water evaporator comprises a rising film or thermo-siphon evaporator, operating as a single unit, or operating in parallel, to generate said steam and said blowdown stream.
14. (Original) The method according to claim 1, wherein said heat transfer surfaces are tubular.
15. (Original) The method as set forth in claim 14, wherein said heat transfer surfaces are operated in a vertical position.

16. (Original) The method as set forth in claim 14, wherein said heat transfer surfaces are operated in a horizontal position.

17. (Original) The method as set forth in claim 14, wherein said heat transfer surfaces are designed for enhanced heat transfer.

18. (Original) The process according to claim 1, wherein said produced water evaporator comprises falling film and rising film in a combined process, operating as a single unit, or operating in parallel, to generate said steam and said blowdown stream.

19. (Original) The process as set forth in claim 14 wherein said circulating brine is heated on the interior of the tubes.

20. (Original) The process as set forth in claim 14 wherein said circulating brine is heated on the exterior of the tubes.

21. (Original) The process as set forth in claim 1, further comprising distributing said circulating brine across a first heat transfer surface of at least one of said plurality of heat transfer tubes to generate a steam vapor.

22. (Original) The process as set forth in claim 21, further comprising collecting said steam vapor and directing it to an injection well present in a selected geological formation, to produce an oil and water mixture.

23. (Original) The process as set forth in claim 21, wherein said steam vapor generated is at a pressure ranging from 200 to 1600 psig.

24. (Original) The process as set forth in claim 1, further comprising the step of treating said produced water evaporator blowdown stream in a zero liquid discharge process.

25. (Original) The process as set forth in claim 1, further comprising the step of injecting said produced water evaporator blowdown stream in a deep well for disposal.

26. (Original) The process as set forth in claim 24, wherein said zero liquid discharge comprises a steam driven multiple effect concentration and crystallization evaporator process to generate (a) high quality steam vapor and, (b) a high solute, high suspended solids slurry.

27. (Original) The process as set forth in claim 1, further comprising supplying said water tube boiler with de-ionized makeup water to produce said steam and a high solute containing blowdown stream.

28. (Original) The process as set forth in claim 27, wherein said de-ionized makeup water is produced by a reverse osmosis unit.

29. (Original) The process as set forth in claim 26, further comprising, dewatering said generated suspended solids slurry in a filter press or belt filter and, further comprising, recycling the filtrate back to the crystallization effect of the multiple effect evaporator.

30. (Original) The process as set forth in claim 24, wherein said zero liquid discharge comprises a steam driven crystallizer evaporator process to generate (a) high quality steam vapor and, (b) a high solute, high suspended solids slurry, and, further comprising, dewatering said generated suspended solids slurry in a filter press or belt filter and, further comprising, recycling the filtrate back to the inlet of the crystallizer evaporator.

31. (Original) The process as set forth in claim 27, wherein said de-ionized makeup water is produced by an ion exchange unit.

32. (Original) The process as set forth in claim 28 or claim 31, wherein the feed water utilized for de-ionized makeup water is fresh water.

33. (Original) The process as set forth in claim 2, wherein a portion or substantially all hardness cations are removed in a deionization zone.

34. (Original) The process as set forth in claim 1, wherein said molecular species is silica.

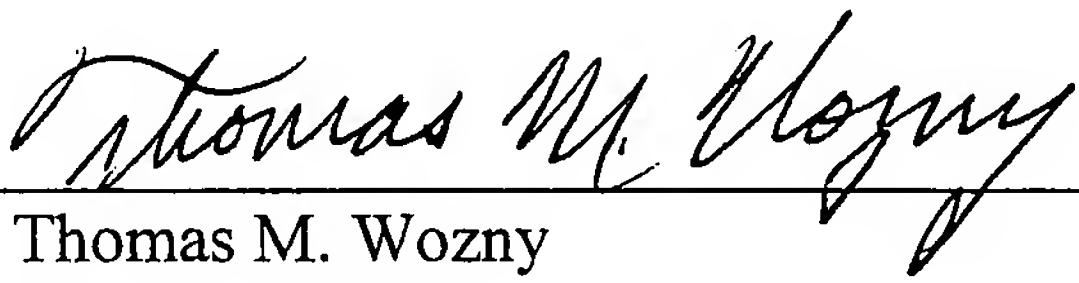
REMARKS

The present Preliminary Amendment is being filed in order to provide an Abstract of the Disclosure as new page 38 of the specification and make of record the claim to priority.

Applicant believes the application is in condition for examination and respectfully requests same.

Respectfully submitted,

ANDRUS, SCEALES, STARKE & SAWALL, LLP

By 
Thomas M. Wozny
Reg. No. 28,922

Andrus, Sceales, Starke & Sawall, LLP
100 East Wisconsin Avenue, Suite 1100
Milwaukee, WI 53202
(414) 271-7590

METHOD FOR PRODUCTION OF HIGH PRESSURE STEAM FROM PRODUCED WATER

ABSTRACT

5 An evaporation based method for generation of high pressure steam from
produced water in the heavy oil production industry. De-oiled produced water is
processed through a high pH/high pressure evaporator driven by a commercial
watertube boiler. The vapor produced by the evaporator is suitable for the steam
assisted gravity drainage (SAGD) method being utilized by heavy oil recovery
installations, without the use of once through steam generators that require
10 extensive chemical treatment, and without requiring atmospheric distillation, which
requires high power consuming compressors. Evaporator blowdown may be
further treated in a crystallizing evaporator to provide a zero liquid discharge
(ZLD) system and, with most produced waters, at least 98% of the incoming
produced water stream can be recovered in the form of high pressure steam.

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
16 June 2005 (16.06.2005)

PCT

(10) International Publication Number
WO 2005/054746 A3

(51) International Patent Classification⁷: F22B 1/08,
E21B 43/24, C02F 1/04

(21) International Application Number:
PCT/US2004/039515

(22) International Filing Date:
24 November 2004 (24.11.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/525,578 26 November 2003 (26.11.2003) US

(71) Applicant (for all designated States except US): AQUAT-
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(72) Inventors; and

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KARLAPUDI, RamKumar [IN/US]; 1981 Fox Croft
Lane, Waukesha, WI 53189 (US). SCHOEN, Richard,
M. [US/US]; N67 W29767 Hartling Road, Hartland, WI
53029 (US).

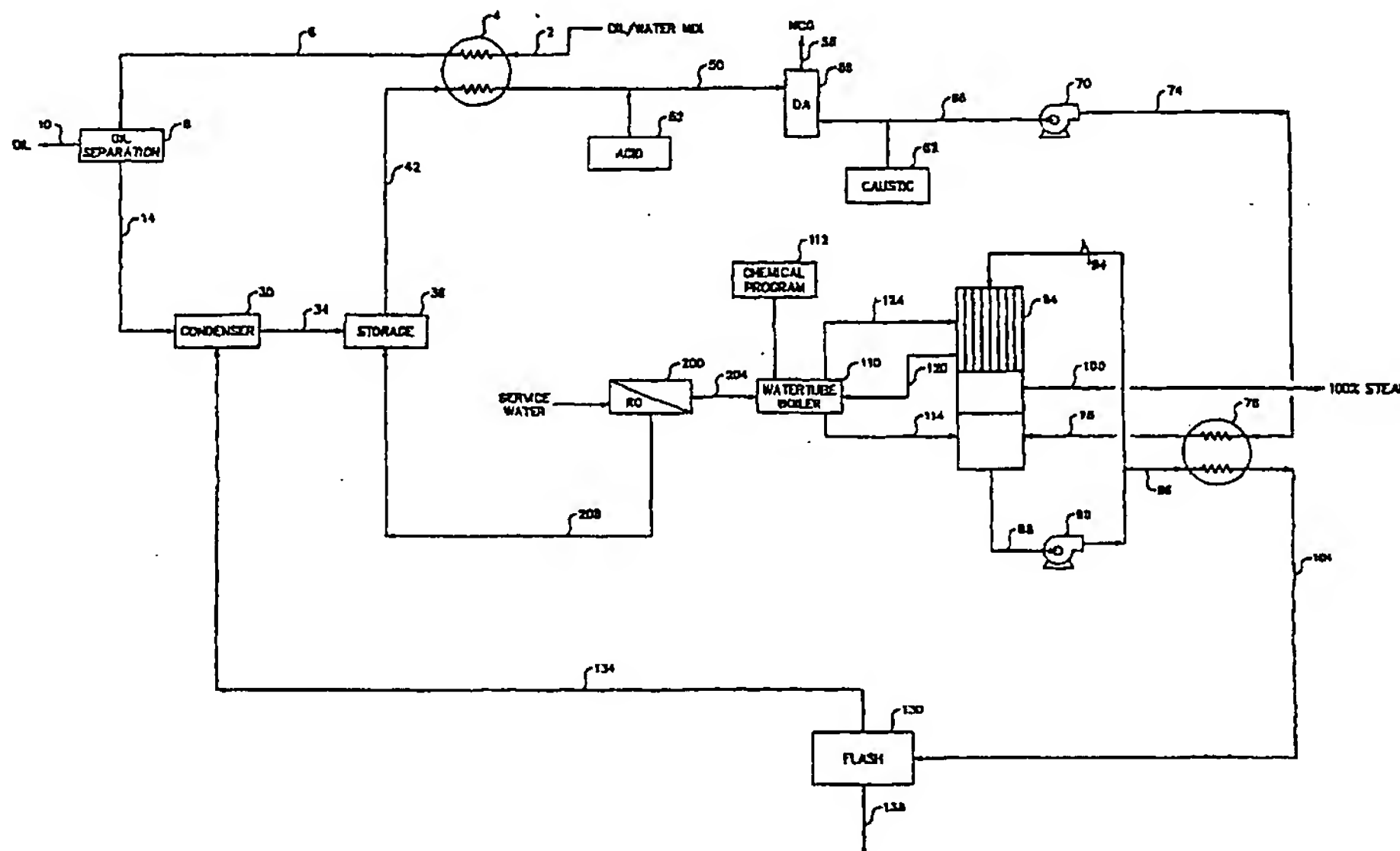
(74) Agent: WOZNY, Thomas, M.; Andrus, Sceales, Starke
& Sawall, LLP, 100 East Wisconsin Avenue, Suite 1100,
Milwaukee, WI 53202-4178 (US).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,
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(54) Title: METHOD FOR PRODUCTION OF HIGH PRESSURE STEAM FROM PRODUCED WATER



(57) Abstract: An evaporation based method for generation of high pressure steam from produced water in the heavy oil production industry. De-oiled produced water is processed through a high pH/high pressure evaporator (84) driven by a commercial watertube boiler (110). The vapor produced by the evaporator is suitable for the steam assisted gravity drainage (SAGD) method being utilized by heavy oil recovery installations, without the use of once through steam generators that require extensive chemical treatment, and without requiring atmospheric distillation, which requires high power consuming compressors. Evaporator blowdown may be further treated in a crystallizing evaporator to provide a zero liquid discharge (ZLD) system and, with most produced waters, at least 98% of the incoming produced water stream can be recovered in the form of high pressure steam.

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2003/127226 A1 (HEINS WILLIAM F) 10 July 2003 (2003-07-10) paragraphs '0014! - '0025!, '0043! - '0056!; figures 4,5 abstract	1-34
A,P	US 6 733 636 B1 (HEINS WILLIAM F) 11 May 2004 (2004-05-11) column 4, line 17 - column 6, line 67; figures abstract	1-34
A	US 4 418 651 A (WYATT ET AL) 6 December 1983 (1983-12-06) column 5, line 22 - column 7, line 5; figures 1,4 abstract	1-34
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Further documents are listed in the continuation of box C.



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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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METHOD FOR PRODUCTION OF HIGH PRESSURE STEAM FROM PRODUCED WATER

TECHNICAL FIELD

[0001] This process relates generally to a method and to a water evaporation system for the treatment of produced waters and high quality steam generation for operations that utilize high-pressure steam to recover oil from geological formations.

BACKGROUND OF THE INVENTION

[0002] Oil producers utilize different means to produce steam for injection into the oil bearing formation. The steam that is injected into the geologic formation condenses by direct contact heat exchange, thus heating the oil and reducing its viscosity. The condensed steam and oil are collected in the producing well and pumped to the surface. This oil/water mixture, once the oil has been separated from it, is what is referred to as 'produced water' in the oil industry.

[0003] Since water can comprise up to 90% of every barrel of oil/water mixture removed from the formation, the recovery and reuse of the water is necessary to control the cost of the operation and to minimize the environmental impact of consuming raw fresh water and subsequently generating wastewater for disposal. Once the decision to recover water is made, then treatment of those produced waters is required to reduce the scaling and/or organic fouling tendency of the water. This treatment generally requires the removal of the hardness and other ions present in the stream, preferably to near zero. As is understood in the art, the 'hardness' causing ions are the combined calcium and magnesium salts in the water to be used in steam generation equipment and is typically expressed as parts per million (ppm) although other terms can be used. While silica is not considered as adding to the hardness value, its presence can also lead to scaling problems if present in other than minimal amounts.

[0004] The traditional method for generation of steam in enhanced oil recovery is to utilize a once-through steam generator (OTSG) in which steam is

generated from a treated feedwater through tubes heated by gas or oil burners. The OTSG feedwater can have a total dissolved solids concentration as high as 12,000 ppm (as CaCO₃ equivalent), but requires a hardness level that is near zero. This method produces a low quality or wet steam, which is 80% vapor and 20% liquid, at pressures ranging from 600 pounds per square inch gauge (psig) up to 2000 psig. This 80% quality steam is separated from the 20% water and then injected into the formation. Either a portion or all of the 20% blowdown is disposed as a wastewater. Another method that has been proposed to obtain the high quality steam requirement is using a water tube boiler instead of the OTSG to generate steam. The water tube boiler, however, requires an even greater amount of feedwater pretreatment than the OTSG to ensure problem free operation. For a comparison of the feedwater requirements for both OTSG and water tube boilers, refer to Figures 6 and 7. There are numerous ways to obtain the feedwater quality required for steam generation, several of which are outlined below for illustration.

[0005] The oil/water mixture coming out of the production well is sent to the primary oil-water separator where substantially all of the oil is separated from the produced water. This separator can be comprised of any known apparatus, but typically, it is comprised of one or more free-water-knock-outs (FWKO), which allow separation of the oil and water by gravity. The separated oil is further treated to remove the last of the water and then sent to storage.

[0006] The separated produced water is sent to a cone bottom tank where heavy solids, such as sand, are allowed to settle out and any remaining oil rises to the top for removal. If any substantial oil remains after this step, one or more induced gas flotation units are utilized to remove substantially all of the oil present in the produced water. Alternately, a de-oiling polymer can be used with a resultant waste oil/solids sludge, which needs further handling for disposal.

[0007] The de-oiled produced water stream is then further treated for reuse. Its constituents are variable but typically it is relatively high in total dissolved solids (TDS), total organic carbon (TOC), hardness, and silica. The water

treatment plant schemes which have heretofore been utilized downstream of the de-oiling zone and upstream of the steam injection well, as well as the equipment which is necessary or desirable to obtain high quality steam at 600 psig, or greater, is the focus of the improvements explained and described in this disclosure.

[0008] Referring to Figure 1, which outlines a typical prior art process used to obtain high quality steam for down hole injection, the raw produced water 6 is sent to a de-oiling process zone 8 and then to a warm lime softener 310. Chemicals 312 such as $\text{Ca}(\text{OH})_2$, Na_2CO_3 , MgO , NaOH , and a coagulant are introduced into the lime softener depending on the reaction desired and a precipitate consisting of hardness and silica is generated. Following the lime softener, a media type filter 324 is utilized to remove the small suspended solids that were not caught up in the lime sludge. The partially softened produced water, still saturated in calcium (as CaCO_3), is then further de-ionized in a weak acid cation (WAC) exchanger 18 which essentially removes all remaining divalent ions. The softened produced water is then sent to the once through steam generator 230, via a conduit that passes through pre-heaters (4 and 76), and 80% quality steam 236 is generated. A steam separator 240 removes the 20% water entrainment and produces high quality steam 100 for down-hole injection in the steam flooding process. The high temperature blowdown 96 from the steam separator is then sent to a series of flash tanks to provide progressively lower steam pressures for other uses. If zero liquid discharge is desired, then the flash steam 134 can be used in a steam driven multiple effect evaporator and crystallizer 140 to obtain a zero liquid discharge (ZLD) system.

[0009] This prior art method is known technology and is considered to be the industry standard. However, it carries with it several disadvantages. These are:

[0010] 1. It has the highest chemical cost of any options

[0011] 2. It has the highest cost for sludge and salt cake disposal requirements

[0012] 3. The OTSG's are limited by the 80% conversion of water into steam

[0013] 4. The OTSG has inherent design problems in terms of tube wetting, fouling, and scaling

[0014] 5. In cold weather operations, the sludge from the lime softener becomes very hard to handle

[0015] 6. In the event of an unscheduled maintenance shutdown, the sludge in the lime softener can quickly set up in a form similar to concrete and become very hard to remove from the system.

[0016] Figure 2 depicts another current prior art process in which the lime soda softening, media filter, and polishing WAC are replaced by a mechanical vapor compressor evaporator (MVC) 244. The de-oiled produced water 14 may be treated with an acid such as hydrochloric (HCl) to lower the pH and destroy any non-hydroxide alkalinity present. Any non-condensable gasses (NCG) 58 present may be removed in deaerator 56. Caustic such as sodium hydroxide (NaOH) 62 may then be added to raise the pH to around 10 or higher. The MVC evaporator 244 produces a low TDS distillate stream 246 that is used to feed the OTSG 230 and the process of generating high pressure steam for down-hole injection is accomplished in the same manner as in Figure 1. In this case, the blowdown 96 from the steam separator 240 is flashed to a steam driven crystallizer 252 which concentrates the brine blowdown 248 from the MVC evaporator 244 and thus provides a ZLD system. The low TDS vapor produced in crystallizer 162 is routed through conduit 166, where it is combined with the liquid portion 138 exiting the flash tank 130, and then to the OTSG feed storage tank 36.

[0017] While this process seems to provide a simple approach to providing high quality water to the OTSG, it has limited applicability in that the concentration of the hardness causing ions, such as calcium and magnesium, must be quite low in the raw produced water. If the hardness ions are not low, then the MVC is limited in the concentration factor obtainable, scale control chemicals are required, or it has to operate in the seeded-slurry mode to avoid calcium sulfate and silica scaling. In the seeded-slurry mode, calcium chloride (CaCl_2) and/or sodium sulfate (Na_2SO_4)

has to be added to the feed stream to ensure that a circulating magma of calcium sulfate (CaSO_4) crystals, typically 3-10% suspended solids (SS), is maintained in the MVC evaporator 244. This circulating magma is used as precipitation sites for the incoming calcium ions and for the co-precipitation of silica. This seeded-slurry mode of operation is aptly taught in U.S. Patent No. 4,618,429.

[0018] The disadvantages to this system are:

[0019] 1. Power consumption is high due to MVC evaporator compressor

[0020] 2. A very large electrical infrastructure is required to supply power to the MVC evaporator compressors

[0021] 3. Suppliers of OTSG equipment are reluctant to design to greater than 80% quality steam even with high quality feed water

[0022] 4. OTSG tube wetting problems

[0023] 5. Applicability is limited to low calcium and low magnesium produced waters due to high pH requirements for silica solubility and even when low, acid cleanings are required to maintain evaporator efficiency by removing the CaCO_3 scale that builds up.

[0024] 6. The evaporator is subject to scaling from low solubility constituents in the evaporator feed like strontium, barium and complexes of metals that occur at high pH operation.

[0025] Figure 3 is yet another prior art process that utilizes a MVC evaporator 244 to pre-treat the de-oiled produced water in the same manner as that shown in Figure 2. In this case though, the high quality distillate 246 from the MVC 244 is cooled in heat exchanger 280 and sent via conduit 284 to a reverse osmosis unit (RO) 290 that removes the volatile TOC from it. The RO permeate 294 is then suitable for use by a high efficiency water tube boiler 110 that will produce high quality steam. The need for a steam separator system and blowdown condensate system is eliminated. Likewise, the inherent problems of an OTSG are thus eliminated and a greater conversion of water to steam is obtained. The

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blowdown from the boiler is directed to the MVC (262). The steam driven ZLD system of the preceding figures has to be eliminated in favor of a MVC driven system as the amount of blowdown from the water tube boiler is insufficient to support a steam driven evaporator. Due to compressor limitations, an MVC crystallizer 268 is also required for final concentration. On some produced waters, notably those with minimal non-volatile TOC, the RO system 290 is not required and the MVC distillate 246 is directed to the watertube boiler 110 without any further treatment. However, this variation has the potential of fouling and scaling the watertube boiler to a greater extent than when distillate post treatment is utilized.

[0026] The advantages of this system are the incorporation of the water tube boiler and a lower operating cost, due to lower fuel consumption, as compared to the MVC/OTSG Figure 2 process.

[0027] The disadvantages of this system include:

[0028] 1. Highest power consumption and highest electrical infrastructure requirements

[0029] 2. High total cost compared to other options

[0030] 3. Multiple types of MVC evaporators are required (pretreatment/blowdown and crystallizer) which complicates operation

[0031] 4. TOC is all rejected to the pretreatment/blowdown and crystallizer MVCs which will likely cause foaming problems that will complicate operation and puts the MVC compressors at risk of damage

[0032] 5. Pretreatment MVC evaporator distillate must be cooled prior to RO treatment and then reheated.

[0033] In summary, the prior art process designs in current use for treating heavy oilfield produced waters for high quality steam generation to be utilized in down-hole steam flooding applications is not entirely satisfactory due to:

[0034] 1. physical chemical treatment processes are usually extensive, require high maintenance and operator interface, and generate large sludge

and regeneration streams that need to be dealt with in accordance with strict environmental regulations,

[0035] 2. large quantities required of expensive treatment chemicals that, in cases, need special safety/handling procedures,

[0036] 3. reliance on low efficiency OTSGs to generate high quality steam at a recovery rate of 80%, water to steam and the associated steam separator and blowdown condensate handling systems,

[0037] 4. inherent OTSG problems with insufficient tube wetting, high heat transfer rates, and tube plugging,

[0038] 5. high power consumption requirements and electrical infrastructure due to the use of vapor compressors,

[0039] 6. treating the entire produced water stream to meet requirements for ASME grade water that can be utilized in a commercial water tube boiler.

[0040] As water is becoming increasingly expensive to treat, or in short supply, or both, it would be desirable to simplify the treatment necessary to generate high quality, high pressure steam and reduce the costs. Finally, it would be clearly desirable to meet such increasingly difficult water treatment objectives with better system availability and longer run times than is commonly achieved today.

[0041] It is believed that no one heretofore has thought it feasible to operate a water tube boiler on deionized water coupled to an evaporator system at high pH and at pressures high enough to provide steam that can be directly used for steam flooding projects. The conventional engineering approach has been to design systems such as those depicted in the prior art Figures 1-3 or to limit the final concentrations to levels that do not cause scaling problems.

[0042] Therefore, a heretofore unaddressed need exists in the heavy oil industry to address the aforementioned deficiencies and inadequacies. Accordingly, it would be advantageous to address the drawbacks to current practice, which

would help both the environment and assist the production facility ownership and operations area in controlling costs.

SUMMARY OF THE INVENTION

[0043] The present invention provides a novel high pressure steam generation method for produced water employing industrial high TDS brine concentration technology that eliminates the need for once through steam generators and power consuming vapor compressors.

[0044] In a unique process for producing high pressure steam vapor, de-oiled produced waters of low hardness and low non-hydroxide alkalinity are injected with a caustic solution to raise the pH prior to high pressure steam generation (HiPVap). In situations wherein scale causing non-hydroxide alkalinity is present in the produced water feed stream, an acid injection system is used to destroy the alkalinity prior to raising the pH for steam generation in the HiPVap.

[0045] The preferred design used in the present invention provides a produced water steam generation plant that overcomes a number of important and serious problems. First, the use of problem prone low efficiency once through steam generators for high pressure steam production is no longer required. Second, the pretreatment requirements of the produced water, prior to high pressure steam generation, are minimized or eliminated entirely. Sludge streams associated with warm lime softening are eliminated. Third, the process as disclosed herein, is completely steam driven and there is no requirement for high energy consuming mechanical vapor compressors or electrical infrastructure. Fourth, controlled levels of multivalent cations, combined with controlled levels of non-hydroxide alkalinity, substantially eliminates the precipitation of scale forming compounds associated with sulfate, carbonate, or silicate anions. Thus, cleaning requirements are minimized. This is important commercially because it enables a water treatment plant to avoid lost water production, which would otherwise undesirably require increased treatment plant size to accommodate for the lost production during

cleaning cycles. Fifth, the preferred high pH operational conditions enable a high degree of ionization to be achieved in various species which are sparingly ionized at neutral or near neutral pH in aqueous solution, such as silica, to enable such species to be concentrated to higher levels before precipitation. Sixth, another benefit to HiPVap operation is the use of industry accepted water tube boilers, the feed to which is not organic laden makeup water. Finally, the HiPVap steam generation process has the benefits of a very high brine recirculation rate to evaporation rate ratio, which results in better heat transfer surface wetting, and a lower temperature difference combined with a lower heat transfer rate across the heat transfer surface than an OTSG operating on the same produced water. The result is a better design with less scaling potential and higher allowable concentration factors.

[0046] OBJECTS, ADVANTAGES, AND NOVEL FEATURES

[0047] A new process for producing high-pressure high quality steam from produced water disclosed herein, and various embodiments thereof, can be applied to the heavy oil industry. Such embodiments are particularly advantageous in that they consume less electrical power, minimize the generation of waste products, utilize waste heat, minimize maintenance, and are superior to current water treatment processes heretofore used in the recovery of oil from tar sands and other heavy oil operations.

[0048] From the abovementioned, it will be observed that one of the significant and major objectives resides in the provision of a novel process, including variations thereof, for the treatment of produced waters, so that such waters can be recovered and re-used in producing steam for use in heavy oil recovery operations.

[0049] Another important objective is to simplify process plant flow sheets by minimizing the number of unit processes required in water treatment trains, which simplifies operations and lowers costs in heavy oil recovery operations.

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[0050] Other important, but more specific objectives reside in the provision of various embodiments of an improved water treatment process for production of high quality steam for down-hole use in heavy oil recovery, which:

[0051] (a) eliminates the requirement for once through steam generators and separation of high pressure steam from residual hot condensates;

[0052] (b) eliminates the generation of softener sludges;

[0053] (c) reduces electrical power consumption by utilizing steam as the energy source instead of mechanical vapor compressors;

[0054] (d) minimizes operation and maintenance labor requirements;

[0055] (e) reduces the capital and operating costs of water treatment equipment; and

[0056] (f) minimizes chemical additives and associated handling requirements.

[0057] Other important objects, features, and additional advantages of the invention will become apparent to those skilled in the art from the foregoing and from the appended claims, in conjunction with the detailed discussion below and the accompanying drawing.

[0058] BRIEF DESCRIPTION OF THE DRAWINGS

[0059] In the drawings:

[0060] For comparative purposes, all of the prior art examples shown herein incorporate the Zero Liquid Discharge (ZLD) concept as a part of the illustration although, in many current installations, waste disposal is accomplished by deep-well injection. Those skilled in the art will recognize that merely minimizing the blowdown stream without the use of a dewatering device may, on certain occasions, also qualify the system as ZLD. The high pressure, high efficiency evaporation method defined herein is site specific wherein individual process steps are customized to fit the specific feed water, and needs of the customer. For that reason, all possible embodiments of this novel method of water treatment are not

illustrated and, as those skilled in the art can appreciate, other illustrative embodiments would merely reflect variations and rearrangement of some components without affecting the spirit or concept of this invention.

[0061] The same identifier will reference identical features depicted in each of the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0062] In the drawings:

[0063] FIG. 1 is a schematic diagram that shows a prior art process, specifically a generalized process flow diagram for one typical physical-chemical water treatment process used in steam assisted gravity drainage (SAGD) heavy oil recovery operations.

[0064] FIG. 2 is a schematic diagram that shows a prior art process, specifically a generalized process flow diagram wherein the physical-chemical water treatment method is replaced by a mechanical vapor compression (MVC) process to supply purified water to a once through steam generator (OTSG) used in steam assisted gravity drainage (SAGD) heavy oil recovery operations.

[0065] FIG. 3 is a schematic diagram that illustrates a prior art process in which the distillate from a mechanical vapor compression (MVC) method is further treated in reverse osmosis (RO) equipment that enables replacing a once through steam generator (OTSG) with a commercial packaged boiler in steam assisted gravity drainage (SAGD) heavy oil recovery operations.

[0066] FIG. 4 is a schematic diagram that shows one embodiment of the novel steam generation process disclosed and claimed herein, illustrating the use of the process for high pressure steam production with produced waters low in hardness and alkalinity in steam assisted gravity drainage (SAGD) heavy oil recovery operations.

[0067] Fig. 5 is a schematic diagram that illustrates another embodiment of the novel steam generation process disclosed and claimed herein, illustrating the

use of the HiPVap process on produced waters classified as high in hardness and carbonate alkalinity ions.

[0068] FIG. 6 is a table that shows the typical feedwater quality requirements for steam generators which produce steam in the 1000 pounds per square inch gauge (PSIG), or thereabouts, for once through steam generator installations.

[0069] FIG. 7 is a table that shows the typical feedwater quality requirements for watertube boilers which produce steam in the 1000 pounds per square inch gauge (PSIG), or thereabouts, for watertube boiler installations.

[0070] FIG. 8 is a graph that details the ionization of silica as a function of pH.

[0071] The foregoing figures, being merely exemplary, contain various elements that may be present or omitted from actual process implementations depending upon the circumstances. An attempt has been made to draw the figures in a way that illustrates at least those elements that are significant for an understanding of the various embodiments and aspects of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0072] Heavy oil recovery operations have increasingly incorporated the steam assisted gravity drainage (SAGD) method to recover oil from tar sand and other networks. In this method the injected steam is more efficiently utilized as 100% quality (i.e., no liquid water entrained with the steam) in contrast to older methods in which an 80% steam/20% water mixture was used for steam flooding of the oil field. However, the once through steam generators (OTSG) in standard use are designed to generate 80% quality steam which then requires the use of steam separators to remove the entrained water portion to provide 100% quality steam for down-hole injection. The use of an OTSG to supply the 100% quality steam required for steam flooding leaves the high pressure high temperature liquid portion that needs to be handled and disposed of. In some cases it can be utilized for other steam consumers by using a sequential arrangement of flash tanks, each providing a

lower pressure steam, but ultimately resulting in a liquid stream that had to be disposed of.

[0073] Heavy oil recovery operators are now looking at commercial water tube boilers to generate the 100% steam quality required. This became the desired next step since water tube boilers are designed to provide high purity steam at the pressures required for steam flooding, whereas the installation, operating, and maintenance expenses are lower than OTSGs, and the high efficiency of the water tube boiler results in a small blowdown stream that requires disposal. However, the use of a water tube boiler required a more extensive water pretreatment process as the feedwater requirements are much stricter than for an OTSG. Refer to FIG. 6 and FIG.7 for a comparison of the feedwater characteristics required for the water tube boiler installation in comparison to the OTSG. The industry recognizes that the only way to achieve the water quality required for water tube boilers is to remove the dissolved solutes and TOC (Total Organic Carbon) present in produced waters. This level of pre-treatment requires membrane separation and/or evaporative process. Cooling and subsequent reheating of the produced water are required for membrane systems due to their temperature limitations. Also, the evaporation processes that have been considered (reference Figures 2 and 3) are energy intensive.

[0074] The invention disclosed herein provides a novel integrated process for generating high pressure steam from produced water. The energy that would normally only be used once to generate injection steam is used twice in this process. The first use of the energy is the generation of steam from high purity water in a water tube boiler. The second use is the generation of injection steam from produced water. The generation of injection steam from produced water is accomplished by utilizing a high pressure, high efficiency HiPVap process. This overcomes the disadvantages of the low efficiency OTSG, the requirements for treating the full produced water feed stream to ASME quality standards for water tube boilers, and high power consumption by the MVC installations. When

incorporated with the zero liquid discharge (ZLD) in one embodiment, recoveries greater than 98% of the produced water feed stream are attainable at a cost effective price with no liquid streams requiring disposal.

[0075] Present day state of the art steam generation, either OTSG or watertube boiler, is limited on how much water can be recovered by scale causing ions, such as hardness and silica, which are inherent in these waste streams, total organic carbon (TOC), and maximum total dissolved solids (TDS) allowable in the feed stream. The additions of expensive scale inhibiting agents or scale control methods are beneficial but still have their limits of usefulness. Evaporators that are used as industrial brine concentrators overcome the TDS limitations with their built in high solids capability and heat transfer surface wetting design. They can also handle high TOC loadings but volatile TOC carries over with the generated vapor which, when condensed, passes into any downstream users of the distillate produced causing scaling and/or fouling problems.

[0076] The present invention provides a novel process to overcome these limitations and recover more of the produced water for steam generation than was previously possible by providing a high pH scale free environment in a high pressure, high efficiency HiPVap process that incorporates the high solutes capability of industrial brine concentrators. Volatile TOC does not present a problem as it is carried out with the high pressure steam vapor and sent to the borehole for steam injection. In addition, the HiPVap process does not require any additional energy to produce high pressure injection steam, as compared to conventional OTSG systems, and uses significantly less energy than the current MVC evaporative technologies.

[0077] Although it may seem impractical to use steam to generate steam, the practice has positive benefits when applied as disclosed herein. Of prime importance is the fact that both the industrial high pressure evaporator and the watertube boiler are being operated in the environments that they were originally designed for; i.e. a high TDS brine concentrating evaporator coupled with a high

pressure high purity ASME grade watertube boiler. This leads to equipment reliability and reduced costs. The cost reductions can be broken down into lower operating costs, since there is no requirement for mechanical vapor compressors, and lower water pretreatment capital costs, since there is not a requirement for extensive water conditioning associated with changing a produced water into ASME quality water.

[0078] Attributes that characterize the high pressure, high efficiency evaporator (HiPVap) process design and operation are:

[0079] Generation of high quality steam at pressures ranging from 200 to 1600 psig without the use of a low efficiency once through steam generator (OTSG).

[0080] The ratio of evaporation to recirculation of produced water inside the HiPVap unit is very low, thus the heat transfer surface stays very well wetted and scaling potential along with dry spots is minimized.

[0081] Lower power consumption and lower electrical infrastructure costs as electrically driven steam vapor compressors are not required.

[0082] Time proven conservative industrial design for the evaporation of high TDS streams with high organic levels.

[0083] Elimination of lime softening waste streams which are difficult to handle in cold climates.

[0084] Simplified pretreatment process for de-oiled produced water prior to steam generation.

[0085] Very high solubility of weak acid anions such as silica when operating at a high pH.

[0086] Very high achievable concentration factors (recovery--ninety percent (90%) or higher recovery can be achieved).

[0087] Cleaning frequency is substantially reduced.

[0088] Addition of scale inhibitors is virtually eliminated.

- [0089]** Corrosion potential is reduced by operation at high pH thus allowing the use of low cost materials of construction.
- [0090]** Reduced overall operating cost, compared to conventional produced water recovery and steam generation systems.
- [0091]** Reduced overall capital cost, compared to conventional produced water recovery and steam generation systems.
- [0092]** The HiPVap process is site-specific. Individual process steps are customized to fit the particular produced water at a given site. Regardless of the difference in the pretreatment process for different sites, one process parameter is common for all applications, namely that the HiPVap system is operated at the highest feasible blowdown pH. This factor enables the circulating solution to provide a low corrosion potential, high silica tolerant, and non-fouling organic environment at the heat transfer surface.
- [0093]** With reference to the various figures, produced water feed stream 14 will typically contain soluble and insoluble, organic and inorganic components. The inorganic components can be salts such as sodium chloride, sodium sulfate, calcium chloride, calcium carbonate, calcium phosphate, barium chloride, barium sulfate, and other like compounds. Metals such as copper, nickel, lead, zinc, arsenic, iron, cobalt, cadmium, strontium, magnesium, boron, chromium, and the like may also be included. Organic components are typically dissolved and emulsified hydrocarbons such as benzene, toluene, phenol, and the like.
- [0094]** Produced waters utilized for production of steam additionally include the presence of silicon dioxide (also known as silica or SiO_2) in one form or another, depending upon pH and the other species present in the water. For evaporator systems, scaling of the heat transfer surface with silica is to be avoided. This is because (a) silica forms a relatively hard scale that reduces productivity of the evaporator, (b) it is usually rather difficult to remove, (c) the scale removal process produces undesirable quantities of spent cleaning chemicals, and (d) cleaning cycles result in undesirable and unproductive off-line periods for the

equipment. Therefore, regardless of the level of silica in the incoming raw feed water, operation of conventional evaporation processes, without a scale control method such as preferential deposition seeded slurry, generally involves concentration of SiO_2 in the high solids stream to a level not appreciably in excess of 150 ppm of silica (as SiO_2). This requires that evaporator systems be operated at lowered concentration factors (recovery rates) to prevent silica concentration in the blowdown stream from exceeding solubility limits. Seeded slurry systems can be taken to concentration factors that surpass the solubility of silica but rely on seed management procedures and are still prone to scaling of the evaporator heat transfer surfaces.

[0095] It is commonly understood that the solubility of silica increases with increasing pH, and that silica is quite soluble in high pH aqueous solution. The increase in silica solubility is basically proportional to the change in ionization as increased ionization results in the soluble silicate ion being the dominant species. The solubility is not directly proportional because even un-dissociated silica exhibits some solubility in aqueous solutions, typically up to about one hundred twenty (120) ppm to one hundred sixty (160) ppm, depending upon temperature and other factors. In comparison, it has been demonstrated that silica solubility at pH 11 is in excess of one thousand five hundred (1,500) ppm at ambient temperature; silica is increasingly soluble as temperature and/or pH increases.

[0096] Silica is very weakly ionized when in neutral or near neutral aqueous solutions and is generally considered to exist as un-dissociated (meta/ortho-) silicic acid (H_4SiO_4) in most naturally occurring waters with a pH of up to about 8. The dissociation constant (pKa) value for the first stage of dissociation of silica has been reported at approximately 9.7, which indicates that silica is approximately fifty percent (50%) ionized at a pH of 9.7; the other fifty percent (50%) remains as un-dissociated (ortho) silicic acid at that pH. A graphical representation of the relationship between pH and the percent silica ionization is shown in FIG. 8. Clearly, it would be advantageous, where silica ionization is desired, to operate at a

pH in excess of 10, and more preferably, in excess of 11, and yet more preferably, in excess of 12 where the entire silica molecule is present as a soluble silicate ion.

[0097] Therefore, increasing the pH of the HiPVap process thus provides the major benefit of increased silica solubility. To gain maximum benefit from silica ionization at high pH, the HiPVap system should be operated at a pH as high as possible. Preferably, the evaporator system is operated at a pH of about 10.5 or above, and more preferably, at a pH of 11 or higher.

[0098] By maintaining hardness and non-hydroxide alkalinity at levels which effectively avoid formation of scale at a selected pH for HiPVap process, the concentration of SiO₂ in the HiPVap blowdown stream can be safely increased to at least 5500 ppm, or more. This is accomplished by raising the pH of the produced water fed to the HiPVap system and without the use of silica scale inhibition chemicals or control methods.

[0099] The novel process disclosed herein is situated between the oil separation zone, 8 in the various figures, and the steam injection well used for steam flooding in oil recovery installations. The separated and de-oiled produced water 14, typically with 10 to 20 ppm residual oil, is analyzed for calcium carbonate scale forming potential by use of scale indexes such as the Langelier Saturation Index, the Stiff-Davis Index, and other solubility tables. These indexes, as is known to those with ordinary skill in the art and to whom this specification is directed, take as input the calcium, magnesium, alkalinity, pH, and temperature of operation to determine what amount, if any, of the scale causing ions present in the produced water must be reduced for scale free operation. Other tables, based on calcium sulfate and silica, are also used to determine the solubility levels and concentration factors attainable with these compounds in the produced water stream. After determining the scaling potential of the produced water, an embodiment of this novel process is chosen that will ensure scale free operation at the concentration factor required.

[00100] Referring to FIG. 4 or FIG. 5, following any produced water conditioning, as determined by the appropriate indexes and solubility charts, the herein disclosed novel high pressure, high efficiency HiPVap 84 must be operated in such a manner that the pH of the blowdown is approximately, but preferably not higher than, 12.5. The selected pH is based on the amount of silica in the produced water feed stream along with the concentration factor required and may be lower, but not lower than 10.5, depending on site specific design conditions.

[00101] FIG. 4 represents the HiPVap process as it would be incorporated into a SAGD application with typical produced water containing low hardness and low alkalinity solutes. The necessary pretreatment and conditioning prior to the HiPVap process is accomplished by the addition of acid 52, such as sulfuric or hydrochloric, when necessary and or appropriate, to lower the pH sufficiently to convert bound carbonate alkalinity to gaseous carbon dioxide. The carbon dioxide along with other non-condensable gasses (NCG) such as oxygen and nitrogen are then removed in the HiPVap deaerator 56. Following the deaerator 56, the produced water feed stream is then conditioned by the addition of caustic 62, such as sodium hydroxide or potassium hydroxide, to a pre-selected pH prior to the HiPVap 84 process.

[00102] In the HiPVap 84, the treated and conditioned produced water 78 mixes with and dilutes the concentrated high solids stream present in line 88. This stream is recirculated with high pressure recirculation pump 90 and a small portion is removed as HiPVap blowdown through line 96 on each pass through the HiPVap 84. The solutes in the produced feed water are concentrated in HiPVap 84 by removing water from the diluted recirculating solution in line 94 as it passes over the heat transfer surface. As depicted in Figure 4, the HiPVap utilizes falling thin film evaporation wherein the recirculated stream depicted by line 94 is thinly spread across the inner, or first, surface of a plurality of heat transfer tubes. A small portion of water is removed from the thin recirculating stream in the form of steam vapor driven by the high pressure steam in line 124 which is condensing on

the outside of the heat transfer tubes. The water that has been removed, in the form of high temperature steam at the high pressures necessary for injection, and typically with less than 10 ppm (parts per million) of non-volatile solutes, is routed through line 100 directly to the steam injection well.

[00103] A commercial watertube boiler 110 operating on high quality ASME rated feed water supplies the high pressure steam, through line 124, that is required to drive the high pressure high efficiency HiPVap 84 wherein the high pressure steam transfers heat by condensing on the second surface of said plurality of heat transfer surfaces. The condensing steam descends by gravity to the bottom of the tubular heat transfer surface and is collected as condensate stream 120 and then returned to the commercial watertube boiler 110 wherein energy is supplied and the condensate is returned to its steam form to keep the evaporation process going.

[00104] A small boiler blowdown stream represented by line 114 is taken from the watertube boiler 110, and directed to the HiPVap 84 for recovery. The blowdown stream 114 is necessary to prevent buildup up of total dissolved solids (TDS) in the boiler due to venting and ensuing makeup water requirement and is typically less than 2% of the boiler capacity.

[00105] Makeup water for the watertube boiler 110 can be supplied by any of various means of producing deionized water. As depicted in Fig. 4, the makeup is supplied through line 204 by a small, high recovery, typically greater than 90%, reverse osmosis (RO) unit 200 that operates on good quality service or well water. Under these circumstances, the RO unit 200 provides high quality ASME grade permeate, which along with the industry standard conventional high pressure boiler chemical program 112, ensures trouble free operation of the watertube boiler 110. In other embodiments, the RO unit 200 can be replaced with an ion exchange column, of various types, to provide the ASME quality water required by watertube boiler 110.

[00106] The just described novel HiPVap process produces a high quality steam at pressures dependent on the individual site designs, typically ranging from

200 to 1600 psig, which satisfies the 100% quality steam requirement needed for SAGD operation at a cost reduction when compared to OTSG and MVC processes. Ideally, and as depicted in Fig. 4 and 5, only one stream, HiPVap blowdown 96 needs to be handled. The blowdown, as represented by line 96, from the HiPVap, 84, can be disposed of by what is known as deep well injection, after flashing 130 to atmospheric pressure, in areas where it is permissible and/or possible, off-site waste disposal facilities, or preferentially by a zero liquid discharge (ZLD) system. The flashed steam 134 is then sent to the condenser 30 for recovery.

[00107] DESCRIPTION OF AN EMBODIMENT WITH ZLD

[00108] Referring to FIG. 5, an alternate embodiment of the present invention for the high pressure high efficiency HiPVap process on produced water is shown. It is a flow diagram for produced water that has been recovered from a steam flood process in which the amount of hardness and carbonate alkalinity are high enough that pre-conditioning is required to lower them to acceptable quantities for HiPVap operation. The zero liquid discharge (ZLD) concept is also illustrated in order to further understand the breadth of the process.

[00109] The production stream 2 coming from the well head containing a mixture of oil and water (e.g., 75% water and 25% oil), at a typical temperature of around 330° F, flows to the oil separation zone 8 after passing through the produced water pre-heater 4. After substantially all oil has been removed, typically to a residual content of 10-20 ppm by means as discussed previously, the produced water, now at a temperature around 190° F, flows via line 14 to the deionization zone 18 which incorporates weak acid cation (WAC) resins operating in the sodium form. In the WAC the calcium and magnesium cations are reduced to non-scaling levels by replacing them with sodium ions.

[00110] After calcium and magnesium removal in the deionization zone 18, the now softened produced water 24 flows to a direct contact condenser 30. In

condenser 30, the produced water mixes with and condenses the steam vapor from the crystallizing effect 162 of the multiple effect ZLD system.

[00111] After the condenser 30, the mixed stream 34 is transferred to buffer storage tank 36 where distillate 186 from the ZLD system is added.

[00112] The outlet 42 from buffer storage tank 36, now at a temperature of about 205° F is pressurized to suppress boiling and routed via line 42 through produced water pre-heater 4, which adds about 100° F to the stream, and then to degasifier 56 through conduit 50. Acid 52 is added, as appropriate and as determined necessary by the different scaling indexes, to the effluent 50 from produced water pre-heater 4 to enhance non-hydroxide alkalinity destruction. Sufficient acid is added to lower the pH where bound carbonates are converted to a free gas carbon dioxide. Then, the carbon dioxide that has been created by acid addition is removed, along with other non-condensable gasses (NCG) 58 such as oxygen and nitrogen, preferably in a flash type degasifier 56 although a forced draft type degasifier could also be utilized.

[00113] Preferably, either hydrochloric (HCl) or sulfuric (H₂ SO₄) acid is used for lowering the pH although other acids will also work. In other embodiments, wherein the different scaling indexes indicate that alkalinity removal is not required for scale free operation at elevated pH, the acid addition 52 and degasifier 56 are not utilized.

[00114] One precaution that should be observed is that both hardness and non-hydroxide forms of alkalinity should be at non-scaling levels in the produced water prior to upward pH adjustment for selected HiPVap operating conditions. Once these conditions are met, then the desired pH increase may be accomplished with any convenient caustic source, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH). Once this pretreatment has been thoroughly accomplished, then a HiPVap system can be safely operated at very high pH levels, in order to take advantage of the aforementioned silica solubility and corrosion resistance.

[00115] The treated and conditioned produced water is pressurized to the selected operating pressure with high pressure pump 70, typically 1000 psig, or greater, and directed to the high pressure high efficiency steam generator (HiPVap) 84 through blowdown heat exchanger 76. A caustic 62 (base) is added, preferably by pumped injection of liquid solution, to increase the pH of the produced feed water 66 to a pre-selected level. The pH of the produced water is raised to a selected pH of at least about 10.0, or preferably to a range between 10 and 11, or otherwise in excess of 11, and most preferably to 12 or more and is maintained, at the selected operating level, in the HiPVap process.

[00116] The HiPVap 84 and water tube boiler 110 operations have been described in detail above and will not be repeated again since there are no changes in the process itself, even with the other embodiments incorporated described here.

[00117] Makeup water for the watertube boiler 110 is supplied through line 204 by a small, high recovery, typically greater than 90%, reverse osmosis (RO) unit 200 that operates on high quality distillate from the multiple-effect ZLD system. Under these circumstances, the RO unit 200 provides high quality ASME grade permeate, which along with the industry standard conventional high pressure boiler chemical program 112, ensures trouble free operation of the water tube boiler 110. The reject stream from the RO unit 200 is routed via line 208 to the crystallizer effect 162 of the ZLD system.

[00118] The high pressure high efficiency HiPVap blowdown represented by line 96 is directed through blowdown heat exchanger 76 where it gives up heat to the incoming produced water feed in line 74. The cooled blowdown in line 104, at a typical temperature of 500° F and at ninety per cent (90%) or less of the incoming produced water flow, containing the concentrated solutes originally present in the produced water 14 along with any chemicals used to lower and raise the pH can be disposed of by the standard approach used at individual sites. This includes flashing to recover lower temperature steam for other purposes and then holding the

liquid portion on-site in waste evaporation ponds, trucking to a waste site, or injection into deep wells.

[00119] In the preferred embodiment as described herein, the blowdown stream depicted as line 104 is directed to the multiple-effect ZLD system as shown in FIG. 5 wherein increased recovery is accomplished. The first step in the ZLD process involves flashing the blowdown 104 to a lower pressure in flash tank 130. The flash tank 130 separates the HiPVap liquid blowdown 104 into a lower temperature steam line 134 and liquid stream 138 which are routed to Effect (1) 142 which constitutes a primary concentrator evaporator. Effect (1) 142 is the first effect of effects (1), effect (2), etc, through effect (N) (wherein N is a positive integer equal to the number of effects) to successively recover a series of lower pressure steam flows which are utilized to drive evaporation in the succeeding effect. The first effects of the ZLD process gradually concentrate the blowdown from evaporator 84 prior to solute crystallization in effect (N) 162. The concentration effects 1, 2, etc. may be falling film or rising film type evaporators while the N effect, or crystallizer, is typically of the forced circulation type.

[00120] The solutes in the recirculated blowdown stream, as represented by line 138, are concentrated by removing water from the recirculating solution as it passes over the heat transfer surface in effect 142. As depicted in FIG. 5, the evaporator utilizes falling thin film evaporation wherein the recirculated stream depicted by line 138 is thinly spread across the inner surface of a plurality of heat transfer tubes. A small portion of water is removed from the thin recirculating stream in the form of steam vapor driven by the flashed steam in line 134 which is transferring heat by condensing on the outside of the heat transfer tubes. The condensing steam descends by gravity to the bottom of the tubular heat transfer surface and is collected as condensate stream 160.

[00121] The condensate stream 160 is routed through effect (2) 152 where it is combined with the distillate 170 from effect (2) 152 and then through effect (N) 162. The combined distillate/condensate 166 from all effects is then routed to the distillate heat exchanger 182 and then to storage 36 via line 186.

[00122] The steam vapor produced in effect (1) 142 is collected and directed to effect (2) 152 via line 144 to provide the driving force for evaporation. Line 148 represents the concentrated blowdown from effect (1) 142 which is recirculated across the heat transfer surface in effect (2) 152 as was described for the preceding effect. The steam vapor 154 generated is routed to effect (N) 162 where it condenses and heats the recirculating solution in a forced circulation heat exchanger. The blowdown from effect (2) 158 is recirculated through the heat exchanger in effect (N) 162 and then flashed into a chamber where the highly concentrated solutes precipitate out of solution.

[00123] Line 178 represents the concentrated blowdown from effect (N) 162 containing precipitated solids that can then be disposed of either by sending it to an on-site waste holding area for disposal or preferably in a solids dewatering device. Typical dewatering equipment consists of various type filter presses or centrifuges in which the suspended solids are removed from the mixed solution by filtration or centrifugal forces. The dewatered solids can then be trucked off either for disposal in a landfill site or, in some cases, sold for their value as inorganic salts. The filtrate is then sent back to the crystallizing effect (N) for further processing. In other installations, as applicable, the blowdown 178 is sent to a spray dryer and any water is removed from the mixed solution by the application of heat resulting in nothing left but salts of various types.

[00124] The vapor produced in the crystallizer effect (N) 162 is routed via conduit 174 to condenser 30 wherein it makes direct contact with the incoming de-oiled produced water 14 prior to storage buffer tank 36.

[00125] The final step in our novel process includes taking a portion of low solute condensate and distillate stream 186 for use as RO feed 196 after passing through heat exchanger 192. The high quality RO feed 196, which does not have any volatile organics, allows the RO unit 200 to produce ASME quality permeate water for feed to the watertube boiler 110.

[00126] It should be noted that the use of a tubular falling film evaporator design for equipment 84, 142, and 152 is provided only for purposes of enabling one skilled into this art to understand the evaporation process and is not intended to limit the process to the use of the same. Those familiar with the art will recognize that other designs, such as, for example, a rising film evaporator, or a natural, mechanical, or forced circulation evaporator, may be alternately utilized with the accompanying benefits and/or drawbacks that may be inherent in the alternative designs.

[00127] In other embodiments, and as suited to meet the particularized needs of a selected produced water chemistry, various forms of hardness removal may be utilized as long as the requirements for a resulting scale free environment in the HiPVap are met. These include a sodium form strong acid cation (SAC) exchange or a partial hardness removal utilizing a SAC exchange process followed by a polishing sodium form WAC or SAC. The benefit gained by SAC exchange is the use of sodium chloride (NaCl) as a regenerant as compared to the two-step sodium form WAC process which requires the use of acid and caustic to effect regeneration to the desired sodium form. Drawbacks of the SAC process are lower efficiencies wherein excess sodium chloride is required for regeneration resulting in a 10% to 15% increase over a WAC process, waste stream quantity for disposal, and hardness removal limitations in applications with TDS in excess of about 3000 ppm. However, there are applications where ease of use and relatively cheap cost of sodium chloride makes the SAC process a better choice than a WAC process as long as the effluent meets the scale free environment requirements for the HiPVap process.

[00128] In yet another embodiment, produced water 14 is first treated in a weak acid cation (WAC) ion exchange unit, operated in the hydrogen form where hardness and bicarbonate alkalinity are simultaneously removed. For those cases where produced water 14 hardness is greater than alkalinity, operation of the weak acid cation ion exchange unit must be facilitated by addition of a source of alkalinity, such as by addition of an aqueous solution of sodium carbonate (Na_2CO_3).

[00129] Regeneration of the resin is accomplished by use of conveniently available and cost effective acid. It is well known by those in the art that regeneration of WAC ion-exchange resins may proceed quite efficiently, at near stoichiometric levels (generally, not more than about one hundred and twenty percent (120%) of ideal levels). Preferably, hydrochloric acid may be used, since in such cases highly soluble calcium chloride would be produced, and the regeneration process would not pose the potential danger of formation of insoluble sulfate precipitates, such as calcium sulfate, even with high strength acids. However, by use of a staged regeneration procedure, i.e., by using a low concentration acid followed by a higher concentration acid, it is possible to reliably utilize other acids, including sulfuric acid (H_2SO_4), while still avoiding undesirable precipitates on the resin. In this manner, hardness ions are solubilized to form soluble salts, which are then eluted from the resin bed.

[00130] ECONOMICS OF HiPVap STEAM GENERATION

[00131] An economic analysis of the prior art systems in comparison to a preferred embodiment (FIG. 5) of the novel process disclosed herein was undertaken to further demonstrate the reduced costs that can be realized in the generation of high pressure steam. The study included the four systems as detailed in Figures 1, 2, 3, and 5 along with the following process assumptions for all cases.

[00132]	Inlet Water Analysis, as mg/l CaCO ₃ , except pH and where noted:			
[00133]	Calcium (Ca)	13	Bicarbonate (HCO ₃)	188
[00134]	Magnesium (Mg)	5	Carbonate (CO ₃)	0.3
[00135]	Sodium (Na)	1579	Sulfate (SO ₄)	0.3
[00136]	Potassium (K)	0.51	Chloride (Cl)	1410
[00137]	Silica (SiO ₂)	180	Iron (Total as mg/l ion)	1.1
[00138]	TDS	2179 as mg/l ion		
[00139]	pH	7.3	Temperature	80° C
[00140]	Oil	10-20 mg/l	Flow Rate	3750 GPM

[00141] Assumptions:

[00142] Produced water from the recovery well is available at 164° C for use within the different processes for heat exchange purposes.

[00143] All systems are zero liquid discharge (ZLD).

[00144] A once through steam generator (OTSG) has a water to steam conversion ratio of 80%.

[00145] Watertube boilers operate with a 2% blowdown rate.

[00146] Operating Cost Assumptions:

[00147] The cost of lime and magnesium oxide is the same.

[00148] The OTSGs and water tube boilers operate at the same efficiency for conversion of fuel absorbed heat. The fuel consumption, per unit heat transferred to the water, of the OTSGs and water tube boilers is the same in all cases.

[00149] Capital Cost Assumptions:

[00150] Scope of supply for all cases includes all equipment, instruments, valves, piping, and structural steel shown within boundaries of block flow diagrams.

[00151] Equipment and costs not included in the cost estimate:

[00152] Water storage tanks

[00153] Control systems (PLC, DCS, etc.)

- [00154] Motor control centers (MCC) transformers, switchgear, etc.
- [00155] Installation cost
- [00156] Infrastructure cost for foundations, underground piping, power systems, etc.
- [00157] Plant life is 30 years.

TABLE 1
UTILITIES

	FIG 1	FIG 2	FIG 3	FIG 5
Power (kw-hr/hour)	3,871	18,665	19,289	3,528

TABLE 2
CHEMICAL CONSUMPTION
(Pounds/day as 100% chemical)

	FIG 1	FIG 2	FIG 3	FIG 5
Hydrochloric Acid (HCl)	6,500	6,200	6,200	8,000
Sodium Hydroxide (NaOH)	7,000	10,200	12,200	12,100
Lime (Ca(OH) ₂)	7695	-	-	-
Magnesium Oxide (MgO)	12,000	-	-	-
Coagulant	50	-	-	-
RO Antiscalant	-	-	200	-

TABLE 3
CAPITAL COST RATIOS

	FIG 1	FIG 2	FIG 3	FIG 5
Capital Cost	1.20	1.25	1.30	1.0

TABLE 4
SLUDGE AND SALT CAKE

	FIG 1	FIG 2	FIG 3	FIG 5
Tons/Day	115	63.6	64.7	65.7

TABLE 5
UNIT PROCESS STEPS REQUIRED FOR STEAM GENERATION

	FIG 1	FIG 2	FIG 3	FIG 5
Warm Lime Softening	X			
Media Filtration	X			
Ion Exchange System	X			X
Mechanical Vapor Compression		X	X	
Primary Reverse Osmosis System			X	
Produced Water Chillers			X	
Produced Water Evaporation		X	X	X
High Pressure Produced Water Pump	X	X	X	X
Once Through Steam Generator	X	X		
Steam Separators for 100% Quality Steam	X	X		
Watertube Boiler			X	X

[00158] As can be seen in Tables 1 and 3, the power consumption and capital cost are lower when the high pressure, high efficiency HiPVap method of steam generation, as presented herein, is incorporated into the steam flooding oil recovery methods in current use. When the lower costs are included with other benefits of the HiPVap process, such as reduced complexity of operation, fewer unit processes as shown in Table 6, and increased corrosion resistance, it becomes apparent that the method, as taught herein, is a cost effective, novel, and new approach to overcoming aforementioned present day state of the art limitations and problems.

[00159] BENEFITS OF HiPVap PROCESS DESIGN AND OPERATION

[00160] Many exemplary and desirable process benefits provided by the HiPVap process design and operation were listed above. Detailed explanations of such benefits include:

[00161] (A) Fewer unit processes

[00162] It can be seen from Table 5 above that the HiPVap process is comprised of fewer individual unit operations than other steam generation processes. In the preferred embodiment as depicted by FIG. 5, the HiPVap process

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consists only of the high pressure evaporator and its accompanying commercial watertube boiler as a source of heat to drive the evaporation process. This feature reduces the complexity of produced water recovery for steam generation and leads to fewer operational and maintenance hours required.

[00163] The elimination of a requirement for a once through steam generator (OTSG) carries with it additional benefits chiefly of which is its designed low water to steam efficiency. This design factor is based on the poor wetting of heat exchange surfaces exhibited in current equipment which, in turn, leads to tube burn out at high temperatures and recovery due to dry spots, and tube plugging. The HiPVap, in contrast, is designed for high salinity high scaling probability waters which, by necessity, requires that heat exchange surfaces be thoroughly wetted at all times. Therefore, the rate of recirculation water over the heat transfer surface is much greater than the rate of steam vapor generation ensuring that dry spots cannot occur and that scaling potential is minimized.

[00164] (B) Reduced Capital Cost

[00165] The lowered corrosion potential that results from operating the HiPVap process with a high pH in the concentrated circulating solution allows the use of lower cost materials for heat transfer tubes or plates and other wetted surfaces that are contacted by the concentrated solution, such as sump walls. This is an important advantage since the costs of these materials have a substantial impact on the capital cost of an evaporator. In most cases the use of high cost duplex and AL6XN (6 per cent minimum molybdenum) type stainless steels, which are normally used in high chloride salt solutions, can be eliminated in favor of lower grade materials such as carbon steel. In addition, fewer individual unit processes result in eliminated equipment and installation infrastructure costs.

[00166] (C) Reduced Operating Cost

[00167] The HiPVap process has a significant advantage over other evaporative processes in that high energy consuming mechanical vapor compressors are not required either in the steam generation phase or in the zero

liquid discharge zone. The novel design disclosed herein operates entirely on heat and the recovery of waste heat in liquid blowdown streams. Other systems require large amounts of electrical power input for operation.

[00168] Produced water plant operating costs are also reduced due to minimizing, or eliminating, costly proprietary antiscalants and/or dispersants. Additional savings can be found by eliminating the need for seeded slurry operation at installations where the calcium and sulfate ions are at a high level in the produced water feed stream. Along with the cost of seeding evaporators with calcium sulfate crystals, there is also incurred costs associated with calcium chloride and/or sodium sulfate injected chemicals to provide enough precipitating ions to maintain the seed bed at many installations. Further savings can be realized by the reduction in frequency of cleaning operations, less expensive cleaning chemicals, less downtime for cleaning, and no requirement for costly physical cleaning operations. Still further, if the ZLD option is incorporated, the cost of disposing the waste blowdown is eliminated along with the requirement for freshwater makeup necessary to maintain process flows.

[00169] It will thus be seen that the objects set forth above, including those made apparent from the preceding description, are efficiently attained, and, since certain changes may be made in carrying out the above method and in construction of a suitable apparatus in which to practice the method and in which to produce the desired product as set forth herein, it is to be understood that the invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. For example, while exemplary designs for a falling film high pressure evaporator along with hardness and alkalinity control methods have been illustrated and described, other embodiments are also feasible to attain the result of the principles of the method disclosed herein. Therefore, it will be understood that the foregoing description of representative embodiments of the invention have been presented only for purposes of illustration and for providing an understanding of the invention, and it is not intended to be exhaustive or restrictive,

or to limit the invention to the precise forms disclosed. On the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as expressed in the appended claims. As such, the claims are intended to cover the methods and structures described therein, and not only the equivalents or structural equivalents thereof, but also equivalent structures or methods. Thus, the scope of the invention, as indicated by the appended claims, is intended to include variations from the embodiments provided which are nevertheless described by the broad meaning and range properly afforded to the language of the claims, or to the equivalents thereof.

CLAIMS

1. A process for generating steam for downhole injection in a steam flood process for oil recovery, said process comprising:

(a) heating a de-oiled produced water stream containing water, dissolved solutes, and dissolved gases, said dissolved solutes further comprising at least one molecular species which is at low ionization levels when in solution at around neutral pH,

(b) raising the pH of said heated, produced water stream to maintain the solubility of said molecular species therein at a selected concentration factor,

(c) pressurizing and directing said produced water stream to a circulating concentrated brine in a produced water evaporator, said evaporator having a plurality of heat transfer surfaces,

(d) distributing said circulating brine across a first surface of at least one of said plurality of heat transfer surfaces to generate a steam vapor suitable for injection into a selected geological formation to fluidize oil,

(e) discharging at least some of said brine as an evaporator blowdown stream,

(f) distributing steam from a watertube boiler across a second surface of at least one of said plurality of heat transfer surfaces to condense said steam as a condensate,

(g) returning said condensate to said watertube boiler for steam production, and,

(h) discharging at least some of said condensate as a boiler blowdown to the produced water evaporator.

2. The process as set forth in claim 1, wherein said dissolved solutes further comprise hardness cations in a quantity that produces a scale deposition on said first surface of said heat transfer surfaces at said selected concentration factor.

3. The process as set forth in claim 1, wherein said produced water stream further comprises at least some non-hydroxide alkalinity.
4. The process as set forth in claim 1, wherein the pH is raised to between 10 and 11 and maintained in said evaporator circulating brine.
5. The process as set forth in claim 1, wherein the pH is raised to between 11 and 12 and maintained in said evaporator circulating brine.
6. The process as set forth in claim 1, wherein the pH is raised to between 12 and 13 and maintained in said evaporator circulating brine.
7. The process as set forth in claim 1, wherein the pH is raised to greater than or at least about 13 and maintained in said evaporator circulating brine.
8. The process according to claim 1, wherein the step of raising the pH is accomplished by addition of an inorganic base in aqueous solution, said base selected from the group consisting of sodium hydroxide, and potassium hydroxide.
9. The process as set forth in claim 3, wherein a portion or substantially all non-hydroxide alkalinity in said produced water stream is removed.
10. The process as set forth in claim 9, wherein the step of removing said non-hydroxide alkalinity, is further comprised of lowering the pH of said produced water stream to release at least some free carbon dioxide.
11. The process as set forth in claim 10, wherein the step of adjusting pH is accomplished by the addition of hydrochloric acid or sulfuric acid.
12. The process according to claim 1, wherein said produced water evaporator comprises a falling thin film evaporator, operating as a single unit, or operating in parallel, to generate said steam and said blowdown stream.
13. The process according to claim 1, wherein said produced water evaporator comprises a rising film or thermo-siphon evaporator, operating as a single unit, or operating in parallel, to generate said steam and said blowdown stream.
14. The method according to claim 1, wherein said heat transfer surfaces are tubular.

15. The method as set forth in claim 14, wherein said heat transfer surfaces are operated in a vertical position.

16. The method as set forth in claim 14, wherein said heat transfer surfaces are operated in a horizontal position.

17. The method as set forth in claim 14, wherein said heat transfer surfaces are designed for enhanced heat transfer.

18. The process according to claim 1, wherein said produced water evaporator comprises falling film and rising film in a combined process, operating as a single unit, or operating in parallel, to generate said steam and said blowdown stream.

19. The process as set forth in claim 14 wherein said circulating brine is heated on the interior of the tubes.

20. The process as set forth in claim 14 wherein said circulating brine is heated on the exterior of the tubes.

21. The process as set forth in claim 1, further comprising distributing said circulating brine across a first heat transfer surface of at least one of said plurality of heat transfer tubes to generate a steam vapor.

22. The process as set forth in claim 21, further comprising collecting said steam vapor and directing it to an injection well present in a selected geological formation, to produce an oil and water mixture.

23. The process as set forth in claim 21, wherein said steam vapor generated is at a pressure ranging from 200 to 1600 psig.

24. The process as set forth in claim 1, further comprising the step of treating said produced water evaporator blowdown stream in a zero liquid discharge process.

25. The process as set forth in claim 1, further comprising the step of injecting said produced water evaporator blowdown stream in a deep well for disposal.

26. The process as set forth in claim 24, wherein said zero liquid discharge comprises a steam driven multiple effect concentration and crystallization evaporator process to generate (a) high quality steam vapor and, (b) a high solute, high suspended solids slurry.

27. The process as set forth in claim 1, further comprising supplying said water tube boiler with de-ionized makeup water to produce said steam and a high solute containing blowdown stream.

28. The process as set forth in claim 27, wherein said de-ionized makeup water is produced by a reverse osmosis unit.

29. The process as set forth in claim 26, further comprising, dewatering said generated suspended solids slurry in a filter press or belt filter and, further comprising, recycling the filtrate back to the crystallization effect of the multiple effect evaporator.

30. The process as set forth in claim 24, wherein said zero liquid discharge comprises a steam driven crystallizer evaporator process to generate (a) high quality steam vapor and, (b) a high solute, high suspended solids slurry, and, further comprising, dewatering said generated suspended solids slurry in a filter press or belt filter and, further comprising, recycling the filtrate back to the inlet of the crystallizer evaporator.

31. The process as set forth in claim 27, wherein said de-ionized makeup water is produced by an ion exchange unit.

32. The process as set forth in claim 28 or claim 31, wherein the feed water utilized for de-ionized makeup water is fresh water.

33. The process as set forth in claim 2, wherein a portion or substantially all hardness cations are removed in a deionization zone.

34. The process as set forth in claim 1, wherein said molecular species is silica.

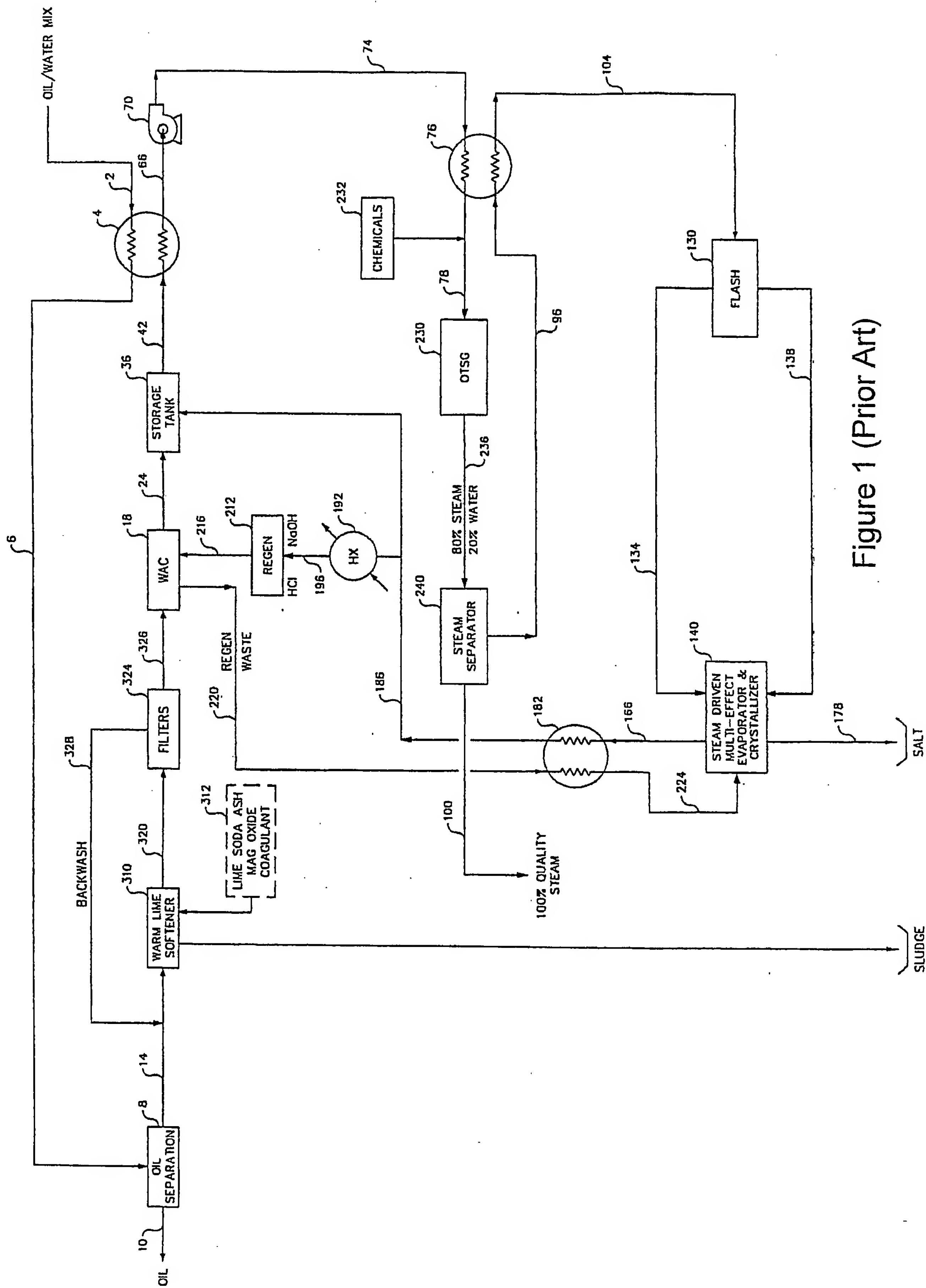
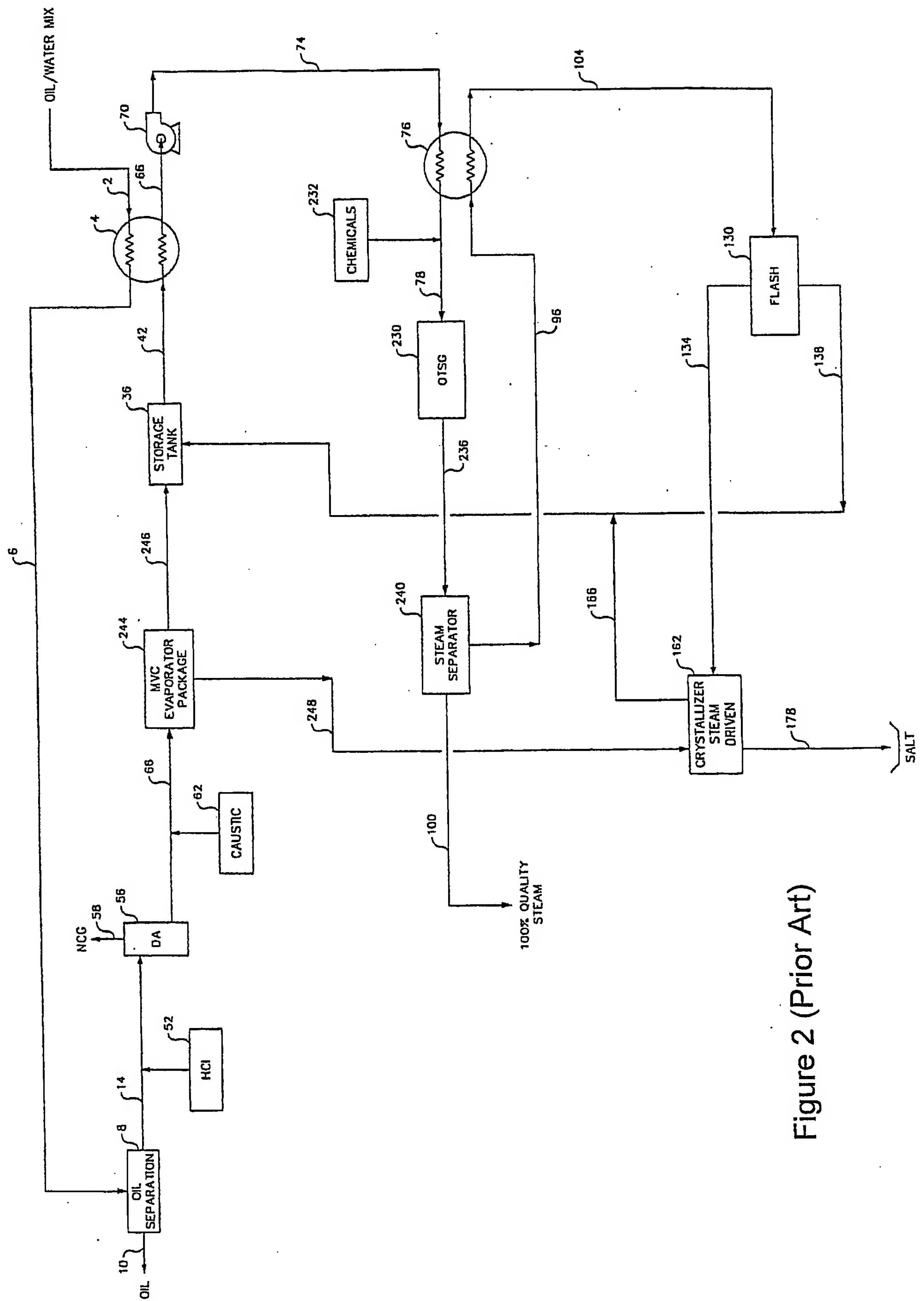


Figure 1 (Prior Art)



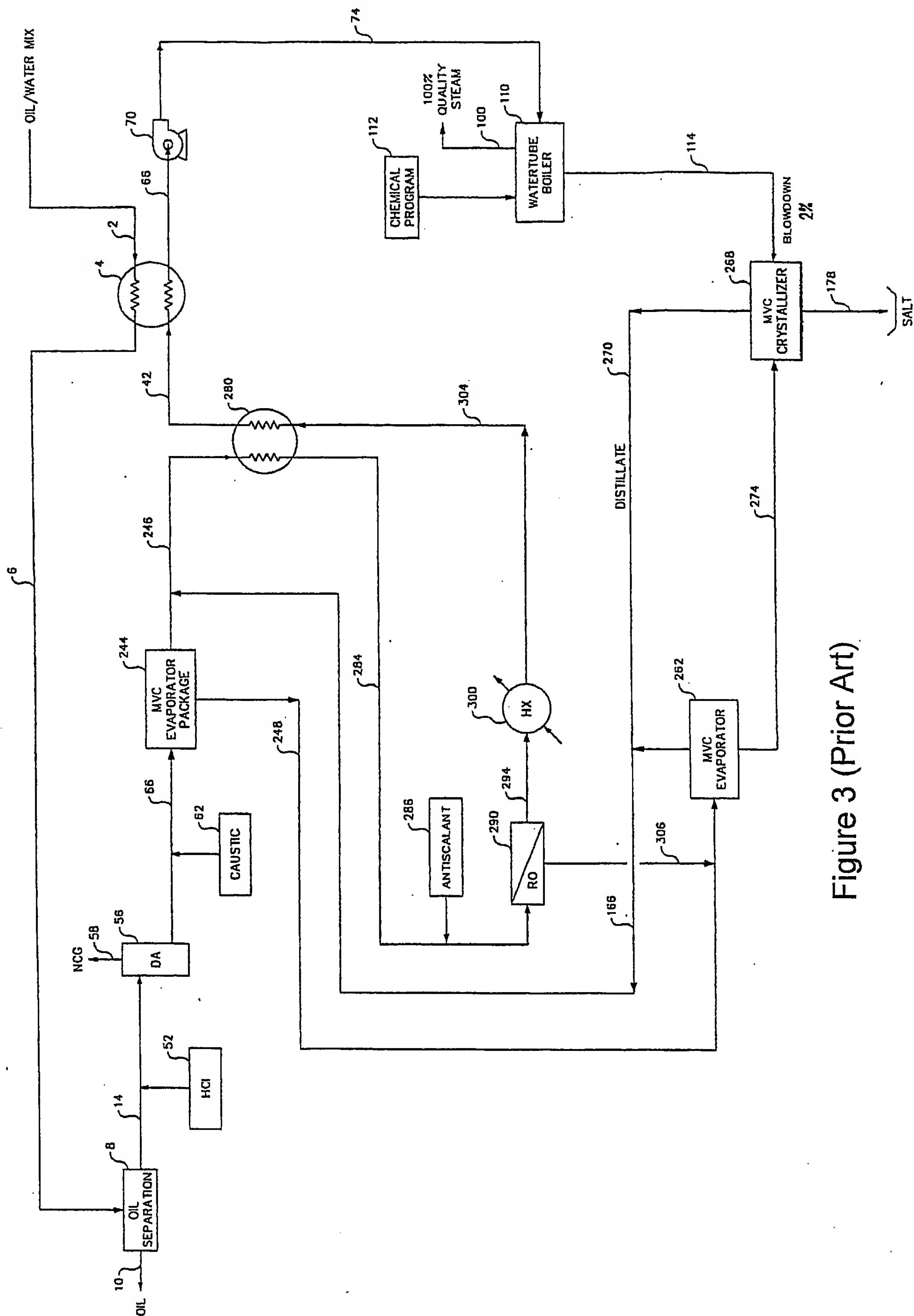


Figure 3 (Prior Art)

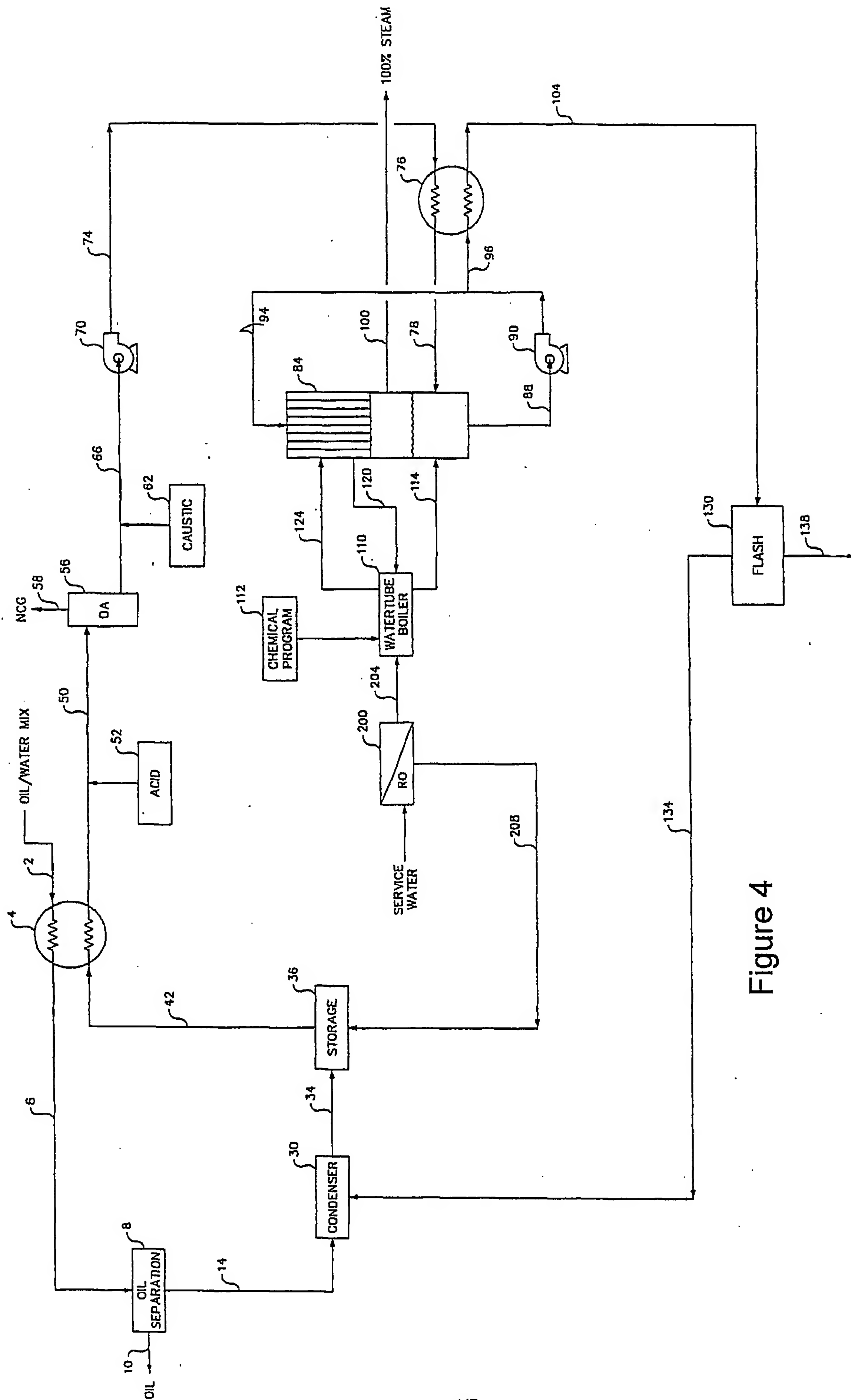


Figure 4

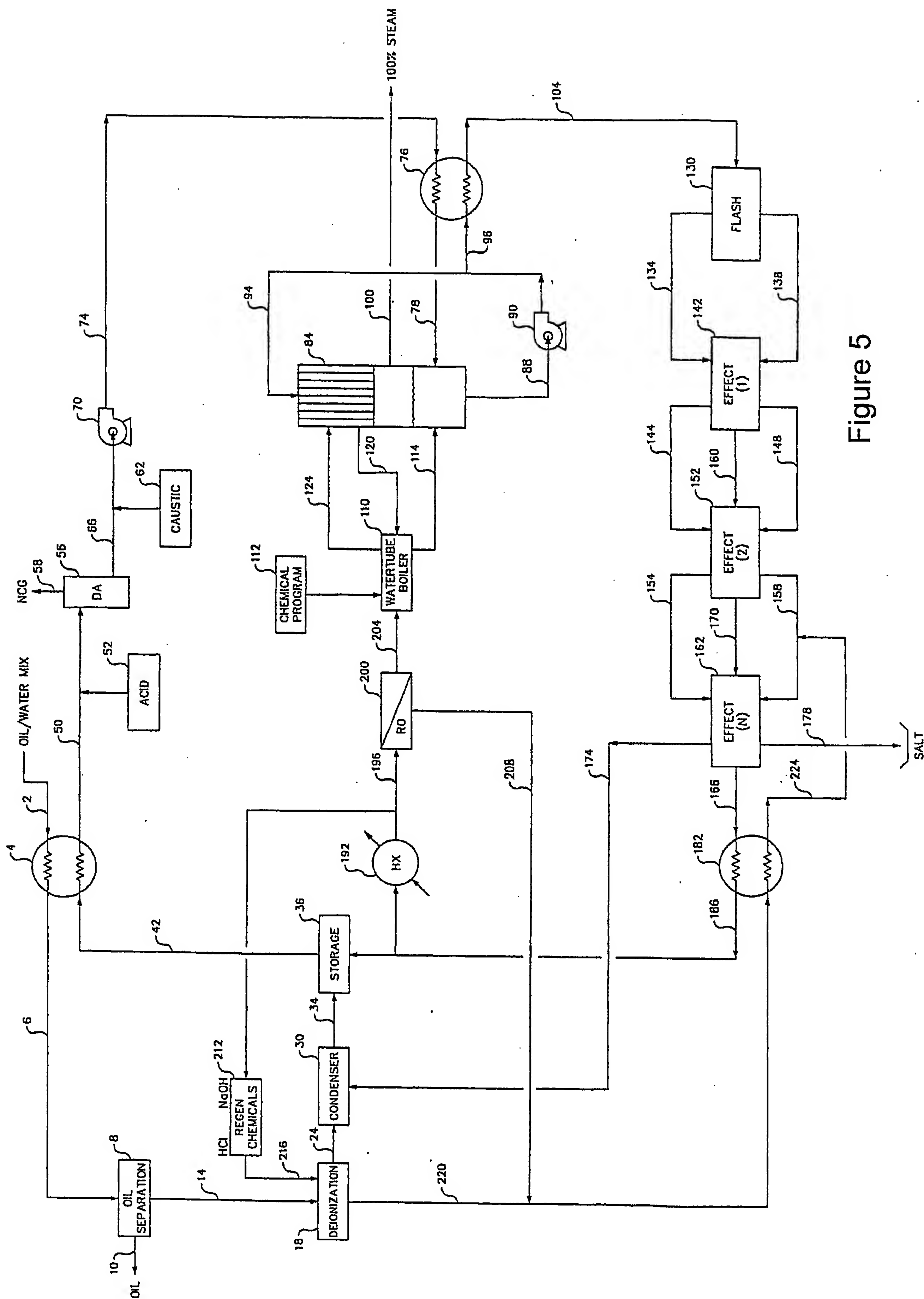


Figure 6

**TYPICAL ONCE THROUGH STEAM GENERATOR
FEEDWATER REQUIREMENTS**

Chlorides	<1000 mg/l
Hardness (as CaCO ₃)	<0.5 mg/l normal <1.0 mg/l maximum
Oil and Grease	<0.5 mg/l normal <1.0 mg/l maximum
TDS	<2500 mg/l
Silica (as SiO ₂)	<80 mg/l
TSS	<1.0 mg/l
Iron (as Fe)	<0.1 mg/l
pH	9.0 – 10.0
H ₂ S	<0.1 mg/l
Oxygen	Zero

Figure 7

**TYPICAL 1000 PSIG WATERTUBE BOILER
ASME FEED and BOILER WATER REQUIREMENTS**

Feedwater	
Hardness (as CaCO ₃)	<0.05 mg/l
Non-Volatile TOC (as C)	<0.20 mg/l
Oil and Grease	<0.20 mg/l
Copper (as Cu)	<0.01 mg/l
pH	8.8 – 9.6
Boiler Water	
Silica (as SiO ₂)	<6 mg/l

Ionization of Silica

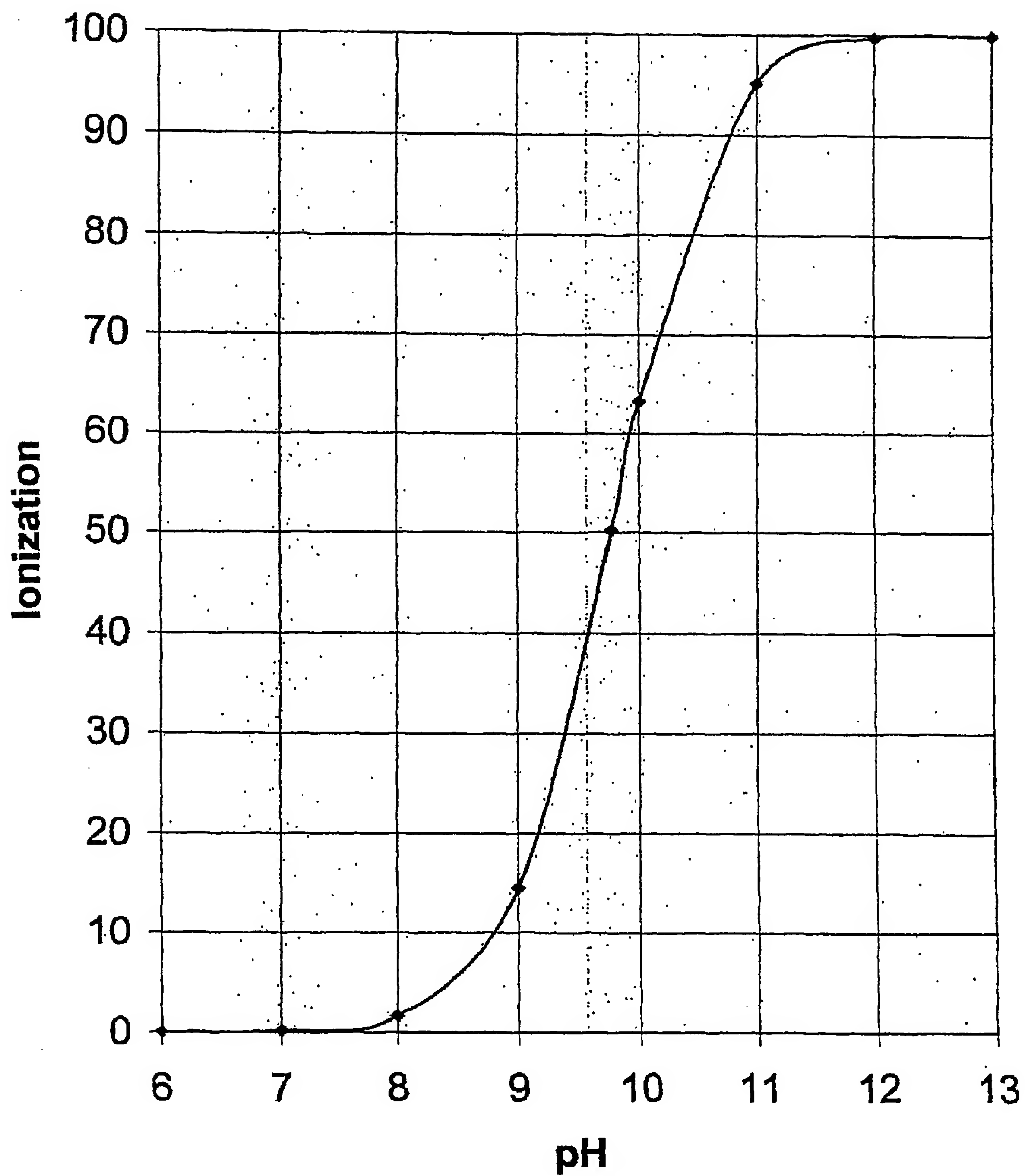


Figure 8

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**DECLARATION
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PATENT APPLICATION**☐ Declaration
Submitted with
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Submitted after
Initial Filing

Attorney Docket Number

4553-00025

First Named Inventor

Keith R. Minnich et al

COMPLETE IF KNOWN

Application Number

10/580,812

Filing Date

Group Art Unit

Examiner Name

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Method for Production of High Pressure Steam from Produced Water

(Title of the Invention)

the specification of which

☐ is attached hereto

OR

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PCT/US2004/039515

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I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under Title 35, United States Code §119(a)-(d) or §365(b) of any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or §365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent, inventor's or breeder's rights certificate(s), or of any PCT international application having a filing date before that of the application on which priority is claimed.

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60/525,578	11/26/2003	

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Attorney Docket Number 4553-00025

DECLARATION

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Name	Registration Number	Name	Registration Number
Daniel D. Fetterley	20,323	Edward R. Williams, Jr.	36,057
George H. Solveson	25,927	Aaron T. Olejniczak	54,853
Gary A. Essmann	29,376	Peter T. Holsen	54,180
Thomas M. Wozny	28,922	Christopher M. Scherer	50,655
Michael E. Taken	28,120	M. Scott McBride	52,008
Joseph J. Jochman, Jr.	25,058	Benjamin R. Imhoff	60,036
Joseph D. Kuborn	40,689	William L. Falk	27,709

☐ Additional attorney(s) and/or agent(s) named on a supplemental sheet attached hereto.

Direct all correspondence to: ☒ Customer Number: 26753 OR ☒ Correspondence address below

NAME	Thomas M. Wozny				
	ANDRUS, SCEALES, STARKE & SAWALL, LLP				
ADDRESS	100 East Wisconsin Avenue				
	Suite 1100				
CITY	Milwaukee	STATE	Wisconsin	ZIP CODE	53202-4178
COUNTRY	U.S.A.	TELEPHONE	(414) 271-7590	FAX	(414) 271-5770

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Name of Sole or First Inventor: ☐ A petition has been filed for this unsigned inventor

Given Name (first and middle [if any]) Keith R.	Family Name or Surname Minnich
Inventor's Signature	Date

Residence: City Pewaukee	State WI	Country US	Citizenship United States
-----------------------------	-------------	---------------	------------------------------

Mailing Address W291 N3821 Round Hill Circle			
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Attorney Docket Number	4553-00025
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DECLARATION	ADDITIONAL INVENTOR(S) Supplemental Sheet
-------------	--

Name of Additional Joint Inventor, if any:		<input type="checkbox"/> A petition has been filed for this unsigned inventor	
Given Name (first and middle [if any]) Mark C.		Family Name or Surname Nicholson	
Inventor's Signature		Date	
Residence: City Pewaukee	State WI	Country US	Citizenship United States
Mailing Address W269 N2740 Lelah Avenue			
City Pewaukee	State WI	Zip 53072	Country US

Name of Additional Joint Inventor, if any:		<input type="checkbox"/> A petition has been filed for this unsigned inventor	
Given Name (first and middle [if any]) RamKumar		Family Name or Surname Karlapudi	
Inventor's Signature		Date	
Residence: City Lake Mary	State FL	Country US	Citizenship India
Mailing Address 1705 Cherry Ridge Drive			
City Lake Mary	State FL	Zip 32746	Country US

Name of Additional Joint Inventor, if any:		<input type="checkbox"/> A petition has been filed for this unsigned inventor	
Given Name (first and middle [if any]) Richard M.		Family Name or Surname Schoen	
Inventor's Signature		Date	
Residence: City Hartland	State WI	Country US	Citizenship United States
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May 9, 2007

Keith R Minnich
W291 N3821 Round Hill Circle
Pewaukee, WI 53072

Re: U. S. Patent Application No. 10/50,812
National Phase of International Application No. PCT/US2004/039515
Andrus Ref: 4553-00025

**METHOD FOR PRODUCTION OF HIGH PRESSURE STEAM
FROM PRODUCED WATER**

Inventors: Keith R Minnich, Mark C. Nicholson, Ram Kumar Karlapudi,
Richard M. Schoen

Dear Keith:

Enclosed for your review is a full copy of U. S. Patent Application Serial No. 10/58,812 as filed May 25, 2006. The application includes the specification, claims, drawings, and Declaration. Also enclosed is a copy of the claims as further revised in a Preliminary Amendment filed May 25, 2006.

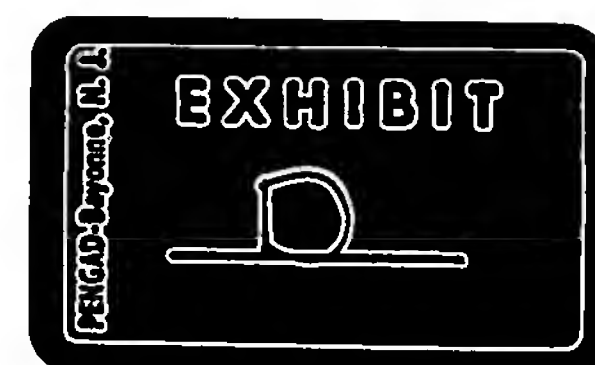
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Mark C Nicholson
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Re: U. S. Patent Application No. 10/50,812
National Phase of International Application No. PCT/US2004/039515
Andrus Ref: 4553-00025

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FROM PRODUCED WATER**

Inventors: Keith R Minnich, Mark C. Nicholson, Ram Kumar Karlapudi,
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Dear Mark:

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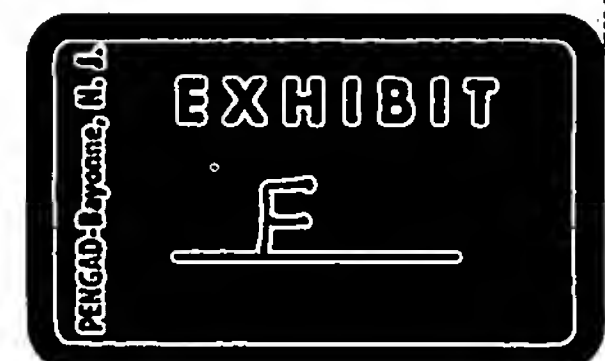
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Dangerous goods (including dry ice) cannot be shipped in FedEx packaging.

7 Payment Bill to:

☒ Sender
Acct. No. in Section
1 will be billed.

☐ Recipient ☐ Third Party ☐ Credit Card ☐ Cash/Check

FedEx Acct. No. Exp. Date
Credit Card No.

Total Packages Total Weight Total Declared Value†
\$.00

†Our liability is limited to \$100 unless you declare a higher value. See back for details. By using this Airbill you agree to the service conditions on the back of this Airbill and in the current FedEx Service Guide, including terms that limit our liability. FedEx Use Only

8 NEW Residential Delivery Signature Options If you require a signature, check Direct or Indirect.

☐ No Signature
Required
Package may be left
without obtaining a
signature for delivery.

☒ Direct Signature
Anyone at recipient's
address may sign for
delivery. Fee applies.

☐ Indirect Signature
If no one is available at
recipient's address, anyone
at a neighboring address may
sign for delivery. Fee applies.

519

Rev. Date 11/05-Part #158779-©1994-2005 FedEx-PRINTED IN U.S.A.-SRS



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Track Shipments Detailed Results

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Tracking number 860072153264
Signed for by J. NICHOLSON
Ship date May 9, 2007
Delivery date May 10, 2007 5:19 PM
Status Delivered
Signature image available [Yes](#)

Destination WAUKESHA, WI
Delivered to FedEx Location
Service type Standard Envelope
Weight 1.0 lbs.

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Reduce future mistakes by using [FedEx Address Checker](#).

[Tracking a FedEx SmartPost Shipment?](#)

Go to [shipper login](#)

Date/Time	Activity	Location	Details
May 10, 2007	5:19 PM Delivered	WAUKESHA, WI	Customer not available or business closed
	4:04 PM At local FedEx facility	WAUKESHA, WI	
	2:11 PM Delivery exception	WAUKESHA, WI	
	8:10 AM On FedEx vehicle for delivery	WAUKESHA, WI	
	7:03 AM At local FedEx facility	WAUKESHA, WI	
	4:44 AM At dest sort facility	MILWAUKEE, WI	
	4:58 AM Departed FedEx location	INDIANAPOLIS, IN	
May 9, 2007	11:44 PM Arrived at FedEx location	INDIANAPOLIS, IN	
	9:09 PM Left origin	PITTSBURGH, PA	
	7:06 PM Picked up	PITTSBURGH, PA	

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Your Name:

Your E-mail Address:

E-mail address

Language

English



Exception updates

Delivery updates



English



English



English



Select format: ☒ HTML ☐ Text ☐ Wireless

Add personal message:

Not available for Wireless or non-English characters.



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3875 Airways Boulevard
Module H, 4th Floor
Memphis, TN 38116

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Memphis, TN 38194-4643

Telephone: 901-369-3600

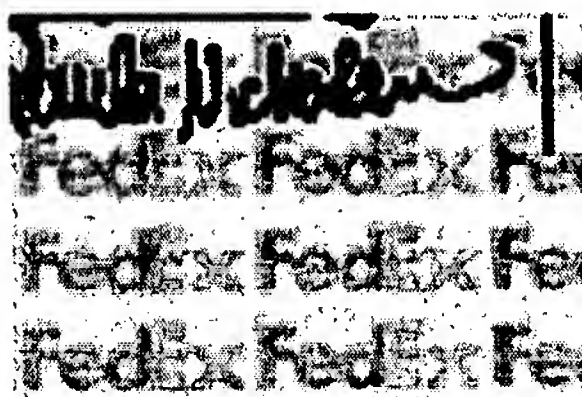
May 29, 2007

Dear Customer:

The following is the proof of delivery you requested with the tracking number **860072153264**.

Delivery Information:

Status:	Delivered	Delivery location:	2001 AIRPORT RD WAUKESHA, WI 53188
Signed for by:	J. NICHOLSON	Delivery date:	May 10, 2007 17:19
Service type:	Standard Envelope		



Shipping Information:

Tracking number:	860072153264	Ship date:	May 9, 2007
		Weight:	1.0 lbs.

Recipient:
MARK C NICHOLSON
-
W 269 N 2740 LELAH AVE
53072 US

Shipper:
LISA SCHOLLAERT
AQUATECH INTERNATIONAL CORP
1 FOUR COINS DR
153171776 US

Thank you for choosing FedEx Express.

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Aquatech International Corporation
One Four Coins Drive
Canonsburg, PA 15317 USA
t) 724 746 5300
f) 724 746 5359
aic@aquatech.com

May 9 2007

Ram Kumar Karlapudi
1705 Cherry Ridge Drive
Lake Mary, FL 32746

Re: U. S. Patent Application No. 10/50,812
National Phase of International Application No. PCT/US2004/039515
Andrus Ref: 4553-00025
**METHOD FOR PRODUCTION OF HIGH PRESSURE STEAM
FROM PRODUCED WATER**
Inventors: Keith R Minnich, Mark C. Nicholson, Ram Kumar Karlapudi,
Richard M. Schoen

Dear Ram:

Enclosed for your review is a full copy of U. S. Patent Application Serial No. 10/58,812 as filed May 25, 2006. The application includes the specification, claims, drawings, and Declaration. Also enclosed is a copy of the claims as further revised in a Preliminary Amendment filed May 25, 2006.

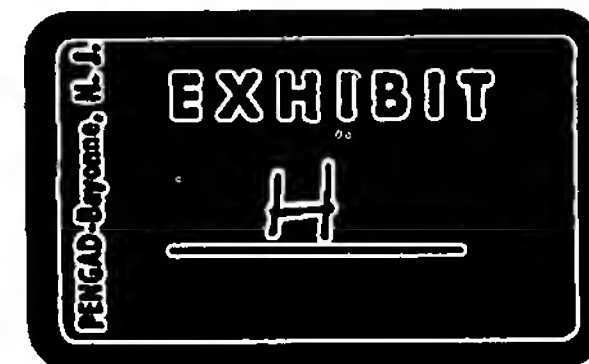
Please sign and date the enclosed Declaration where indicated and return the executed Declaration to me as soon as possible in the enclosed self-addressed, stamped envelope.

If you have any questions, please contact me.

I thank you in advance for your cooperation

Very truly yours,


Lisa Schollaert
Executive Assistant to the CEO





US Airbill

FedEx
Tracking
Number

8600 7215 3242

RETURN → 8600 7215 3253

Form
ID No.

0215

H32

Sender's Copy

1 From Please print and press hard.

Date 09 MAY 2007 Sender's FedEx
Account Number

1029-3958-1

Sender's
Name Lisa SCHOLLAERT

Phone (724) 746-5300

Company AQUATECH INTERNATIONAL CORP

Address 1 FOUR COINS DR

Dept./Floor/Suite/Room

City CANONSBURG

State PA

ZIP 15317-1776

2 Your Internal Billing Reference

First 24 characters will appear on invoice.

OPTIONAL

3 To

Recipient's
Name Ram KUMAR KARLAPUDI 386, 822 8093

Company

Recipient's
Address 1705 CHERRY RIDGE DR.

We cannot deliver to P.O. boxes or P.O. ZIP codes.

Dept./Floor/Suite/Room

Address

To request a package be held at a specific FedEx location, print FedEx address here.

City LAKE MARY

State FL

ZIP 32746

0357346756



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4a Express Package Service

☐ FedEx Priority Overnight
Next business morning.* Friday
shipments will be delivered on Monday
unless SATURDAY Delivery is selected.☐ FedEx 2Day
Second business day.* Thursday
shipments will be delivered on Monday
unless SATURDAY Delivery is selected.

FedEx Envelope rate not available. Minimum charge: One-pound rate.

☒ FedEx Standard Overnight
Next business afternoon.*
Saturday Delivery NOT available.☐ FedEx Express Saver
Third business day.*
Saturday Delivery NOT available.

* To most locations.

Packages up to 150 lbs.

☐ FedEx First Overnight
Earliest next business morning
delivery to select locations.*
Saturday Delivery NOT available.

4b Express Freight Service

☐ FedEx 1Day Freight*
Next business day.** Friday
shipments will be delivered on Monday
unless SATURDAY Delivery is selected.

* Call for Confirmation.

☐ FedEx 2Day Freight
Second business day.** Thursday
shipments will be delivered on Monday
unless SATURDAY Delivery is selected.

Packages over 150 lbs.

☐ FedEx 3Day Freight
Third business day.**
Saturday Delivery NOT available.

** To most locations.

5 Packaging

☒ FedEx
Envelope*☐ FedEx Pak*
Includes FedEx Small Pak,
FedEx Large Pak, and FedEx Sturdy Pak.☐ FedEx
Box.☐ FedEx
Tube☐ Other

* Declared value limit \$500.

6 Special Handling

Include FedEx address in Section 3.

☐ SATURDAY Delivery
NOT Available for
FedEx Standard Overnight,
FedEx First Overnight, FedEx Express
Saver, or FedEx 3Day Freight.☐ HOLD Weekday
at FedEx Location
NOT Available for
FedEx First Overnight.☐ HOLD Saturday
at FedEx Location
Available ONLY for
FedEx Priority Overnight and
FedEx 2Day to select locations.

Does this shipment contain dangerous goods?

One box must be checked:

☐ No☐ YesAs per attached
Shipper's Declaration.☐ YesShipper's Declaration
not required.☐ Dry Ice

Dry Ice, 9, UN 1845

x kg

* Dangerous goods (including dry ice) cannot be shipped in FedEx packaging.

☐ Cargo Aircraft Only

7 Payment Bill to:

Enter FedEx Acct. No. or Credit Card No. below.

☒ Sender
Acct. No. in Section
will be billed.☐ Recipient☐ Third Party☐ Credit Card☐ Cash/CheckFedEx Acct. No.
Credit Card No.Exp.
Date

Total Packages

Total Weight

Total Declared Value†

\$.00

† Our liability is limited to \$100 unless you declare a higher value. See back for details. By using this Airbill you agree to the service conditions on the back of this Airbill and in the current FedEx Service Guide, including terms that limit our liability.

FedEx Use Only

8 NEW Residential Delivery Signature Options

If you require a signature, check Direct or Indirect.

☐ No Signature
Required
Package may be left
without obtaining a
signature for delivery.☒ Direct Signature
Anyone at recipient's
address may sign for
delivery. Fee applies.☐ Indirect Signature
If no one is available at
recipient's address, anyone
at a neighboring address may
sign for delivery. Fee applies.

519

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EXHIBIT

EXHIBIT

I



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Tracking number 860072153242
Signed for by R.KUMAR
Ship date May 9, 2007
Delivery date May 10, 2007 12:42 PM
Status Delivered
Signature image available Yes

Delivered to
Service type
Weight

Residence
Standard Envelope
1.0 lbs.

Wrong Address?

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Date/Time	Activity	Location	Details
May 10, 2007	12:42 PM Delivered		
	8:04 AM On FedEx vehicle for delivery	LONGWOOD, FL	
	7:08 AM At local FedEx facility	LONGWOOD, FL	
	6:17 AM At dest sort facility	ORLANDO, FL	
	4:37 AM Departed FedEx location	MEMPHIS, TN	
May 9, 2007	10:56 PM Arrived at FedEx location	MEMPHIS, TN	
	9:09 PM Left origin	PITTSBURGH, PA	
	7:06 PM Picked up	PITTSBURGH, PA	

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updates

Delivery
updates

English

English

English

English

Select format: ☒ HTML ☐ Text ☐ Wireless

Add personal message:

Not available for Wireless or
non-English characters.

☐ By selecting this check box and the Submit button, I agree to these [Terms and Conditions](#)

[Submit](#)



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Customer Support Trace
3875 Airways Boulevard
Module H, 4th Floor
Memphis, TN 38116

U.S. Mail: PO Box 727
Memphis, TN 38194-4643

Telephone: 901-369-3600

May 29, 2007

Dear Customer:

The following is the proof of delivery you requested with the tracking number **860072153242**.

Delivery Information:

Status:	Delivered	Delivery location:	1705 CHERRY RIDGE DR. 32746
Signed for by:	R.KUMAR	Delivery date:	May 10, 2007 12:42
Service type:	Standard Envelope		

Shipping Information:

Tracking number:	860072153242	Ship date:	May 9, 2007
		Weight:	1.0 lbs.

Recipient:
RAM KUMAR KARLAPUO I386
-
1705 CHERRY RIDGE DR
32746 US

Shipper:
LISA SCHOLLAERT
AQUATECH INTERNATIONAL CORP
1 FOUR COINS DR
153171776 US

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Aquatech International Corporation
One Four Coins Drive
Canonsburg, PA 15317 USA
t) 724 746 5300
f) 724 746 5359
aic@aquatech.com

July 3, 2007

Ms. Danielle L. Hodnicki
Tucker Arensberg, P.C.
1500 One PPG Place
Pittsburgh, PA 15222

Subject: U. S. Patent Application No. 10/580,812
National Phase of International Application No. PCT/US2004/039515
Andrus Ref: 4553-00025
METHOD FOR PRODUCTION OF HIGH PRESSURE STEAM FROM PRODUCED WATER
Inventors: Keith R Minnich, Mark C. Nicholson, Ramkumar Karlapudi, Richard M. Schoen
Assignee: Aquatech International Corporation

Dear Ms. Hodnicki:

I refer to your letter of May 22, 2007 to Frank Frisenda. I enclose a full copy of the U. S. Patent Application Serial No. 10/580,812 as filed May 25, 2006. The application includes the specifications, claims, drawings, and a Declaration to be signed by Keith R Minnich and Mark C. Nicholson.

I also enclose copies of Employment Agreements signed by Mr. Minnich and Mr. Nicholson on August 31, 2000 and August 30, 2000, respectively. Paragraph 7b) of these executed Agreements stipulates that "...upon request of the Company, the Employee shall execute all documents necessary or advisable in the opinion of the Company to direct issuance of patents to the Company or to vest title in the Company to such inventions or discoveries."

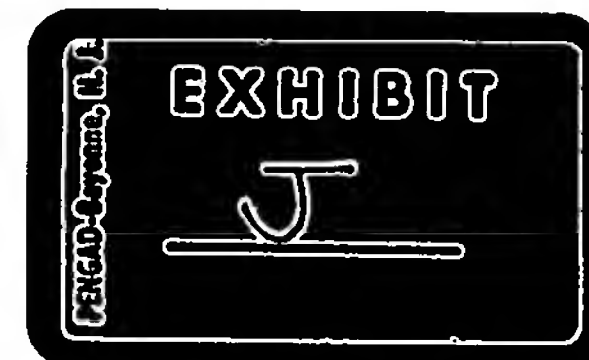
Please have Mr. Minnich and Mr. Nicholson sign and date the Declaration where indicated and return the executed Declaration to me before July 15, 2007.

Alternatively, please have Mr. Minnich and Mr. Nicholson state in writing that they refuse to sign the Declaration for the subject application, and send me such statements by July 15, 2007.

If you have any questions, please contact me.

Very Truly Yours,

Robert D. Pietrala
Vice President and General Council
Aquatech International Corporation



TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A SUBMISSION UNDER 35 U.S.C. 371		ATTORNEY'S DOCKET NUMBER 4553-00025
		U.S. APPLICATION NO. (If known, see 37 CFR 1.5)
INTERNATIONAL APPLICATION NO. PCT/US2004/039515	INTERNATIONAL FILING DATE 24 November 2004	PRIORITY DATE CLAIMED 26 November 2003
TITLE OF INVENTION Method for Production of High Pressure Steam from Produced Water		
APPLICANT(S) FOR DO/EO/US Keith R. Minnich, Mark C. Nicholson, RamKumar Karlapudi, Richard M. Schoen		
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:		
<div style="display: flex; flex-direction: column;"><div style="margin-bottom: 10px;">1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a submission under 35 U.S.C. 371.</div><div style="margin-bottom: 10px;">2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a submission under 35 U.S.C. 371.</div><div style="margin-bottom: 10px;">3. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.</div><div style="margin-bottom: 10px;">4. <input checked="" type="checkbox"/> The US has been elected (Article 31).</div><div style="margin-bottom: 10px;">5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))<div style="margin-left: 20px;"><div style="margin-bottom: 5px;">a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</div><div style="margin-bottom: 5px;">b. <input type="checkbox"/> has been communicated by the International Bureau.</div><div style="margin-bottom: 5px;">c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</div></div></div><div style="margin-bottom: 10px;">6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).<div style="margin-left: 20px;"><div style="margin-bottom: 5px;">a. <input checked="" type="checkbox"/> is attached hereto.</div><div style="margin-bottom: 5px;">b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</div></div></div><div style="margin-bottom: 10px;">7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))<div style="margin-left: 20px;"><div style="margin-bottom: 5px;">a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</div><div style="margin-bottom: 5px;">b. <input type="checkbox"/> have been communicated by the International Bureau.</div><div style="margin-bottom: 5px;">c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</div><div style="margin-bottom: 5px;">d. <input checked="" type="checkbox"/> have not been made and will not be made.</div></div></div><div style="margin-bottom: 10px;">8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</div><div style="margin-bottom: 10px;">9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</div><div style="margin-bottom: 10px;">10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</div></div>		
Items 11 to 20 below concern document(s) or information included:		
<div style="display: flex; flex-direction: column;"><div style="margin-bottom: 10px;">11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</div><div style="margin-bottom: 10px;">12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</div><div style="margin-bottom: 10px;">13. <input checked="" type="checkbox"/> A preliminary amendment.</div><div style="margin-bottom: 10px;">14. <input type="checkbox"/> An Application Data Sheet under 37 CFR 1.76.</div><div style="margin-bottom: 10px;">15. <input type="checkbox"/> A substitute specification.</div><div style="margin-bottom: 10px;">16. <input type="checkbox"/> A power of attorney and/or change of address letter.</div><div style="margin-bottom: 10px;">17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 37 CFR 1.821- 1.825.</div><div style="margin-bottom: 10px;">18. <input type="checkbox"/> A second copy of the published International Application under 35 U.S.C. 154(d)(4).</div><div style="margin-bottom: 10px;">19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</div></div>		



Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)		INTERNATIONAL APPLICATION NO. PCT/US2004/039515		ATTORNEY'S DOCKET NUMBER 4553-00025	
20. Other items or information: A) Small Entity Status					
The following fees have been submitted				CALCULATIONS	PTO USE ONLY
21.	<input checked="" type="checkbox"/>	Basic national fee (37 CFR 1.492(a))..... \$300		\$ 300.00	
22.	<input checked="" type="checkbox"/>	Examination fee (37 CFR 1.492(c))		\$ 200.00	
If the written opinion prepared by ISA/US or the international preliminary examination report prepared by IPEA/US indicates all claims satisfy provisions of PCT Article 33(1)-(4)..... \$0					
All other situations.....\$200					
23.	<input checked="" type="checkbox"/>	Search fee (37 CFR 1.492(b))		\$ 400.00	
If the written opinion of the ISA/US or the International preliminary examination report prepared by IPEA/US indicates all claims satisfy provisions of PCT Article 33(1)-(4)..... \$0					
Search fee (37 CFR 1.445(a)(2)) has been paid on the international application to the USPTO as an International Searching Authority.....\$100					
International Search Report prepared by an ISA other than the US and provided to the Office or previously communicated to the US by the IB..... \$400					
All other situations.....\$500					
TOTAL OF 21, 22 and 23 =				900.00	
<input type="checkbox"/> Additional fee for specification and drawings filed in paper over 100 sheets (excluding sequence listing in compliance with 37 CFR 1.821(c) or (e) or computer program listing in an electronic medium) (37 CFR 1.492(j)). The fee is \$250 for each additional 50 sheets of paper or fraction thereof.					
Total Sheets	Extra Sheets	Number of each additional 50 or fraction thereof (round up to a whole number)	RATE		
- 100 =	/50 =		x \$250.00	\$ 0.00	
Surcharge of \$130.00 for furnishing any of the search fee, examination fee, or the oath or declaration after the date of commencement of the national stage (37 CFR 1.492(h)).				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$ 900.00	
Total claims	34 - 20 =	14	x \$50.00	\$ 700.00	
Independent claims	1 - 3 =	0	x \$200.00	\$ 0.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$360.00	\$ 0.00	
TOTAL OF ABOVE CALCULATIONS =				\$ 1,600.00	
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. Fees above are reduced by ½.				800.00	
SUBTOTAL =				\$ 800.00	
Processing fee of \$130.00 for furnishing the English translation later than 30 months from the earliest claimed priority date (37 CFR 1.492(i)).				\$	
TOTAL NATIONAL FEE =				\$ 800.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				\$	
TOTAL FEES ENCLOSED =				\$ 800.00	
				Amount to be refunded:	\$
				Amount to be charged	\$

- a. ☒ A check in the amount of \$ 800.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. 01.2000 in the amount of \$ _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 01.2000. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the International Application to pending status.

SEND ALL CORRESPONDENCE TO:

Andrus, Scales, Starke & Sawall, LLP, 100 East Wisconsin Avenue, Suite 1100, Milwaukee, WI 53202-4178, (414) 271-7590, Facsimile: (414) 271-5770

CERTIFICATE OF EXPRESS MAIL: I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as EXPRESS MAIL-POST OFFICE TO ADDRESSEE, in an envelope addressed to: BOX PCT COMMISSIONER OF PATENTS, P.O. Box 1450, Alexandria, VA 22313-1450 on May 25, 2006

The Express Mail Label is

EV415015400US

May 25, 2006

Dorothy A. Hauser

Date

Thomas M. Wozny
SIGNATURE

Thomas M. Wozny
NAME

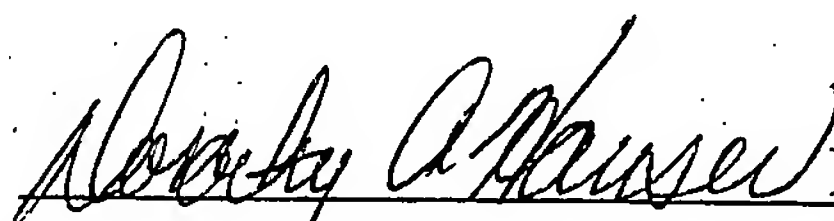
28,922

REGISTRATION NUMBER

EV415015400US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of:)	CERTIFICATE OF EXPRESS MAILING
Keith R. Minnich)	I hereby certify that this correspondence is
Mark C. Nicholson)	being deposited with the United States
RamKumar Karlapudi)	Postal Service with sufficient postage as
Richard M. Schoen)	EXPRESS MAIL in an envelope addressed
)	to: Commissioner for Patents, Alexandria,
Filed Herein)	VA 22313-1450 on this 25th day of May,
)	2006. The Express Mail Label is
International Appl. No.)	EV415015400US.
PCT/US2004/039515)	
International Filing Date:)	
24 November 2004)	
Priority Date Claimed:)	
26 November 2003)	
Method for Production of High Pressure)	
Steam from Produced Water)	
)	
Attorney Docket No. 4553-00025)	

 May 25, 2006
Dorothy A. Hauser Date

SUPPLEMENT TO TRANSMITTAL LETTER

Mail Stop: PCT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

This application is being filed to enter the national stage of the PCT pursuant to 37 C.F.R. §1.495(c). The application includes the specification, at least one claim, and the filing fee. The Declaration is not included. The inventors are:

- 1) Keith R. Minnich
W291 N3821 Round Hill Circle
Pewaukee, Wisconsin 53072
Citizenship: United States
- 2) Mark C. Nicholson
W269 N2740 Lelah Avenue
Pewaukee, Wisconsin 53072
Citizenship: United States

- 3) RamKumar Karlapudi
1981 Fox Croft Lane
Waukesha, Wisconsin 53189
Citizenship: India
- 4) Richard M. Schoen
N67 W29767 Hartling Road
Hartland, Wisconsin 53029
Citizenship: United States

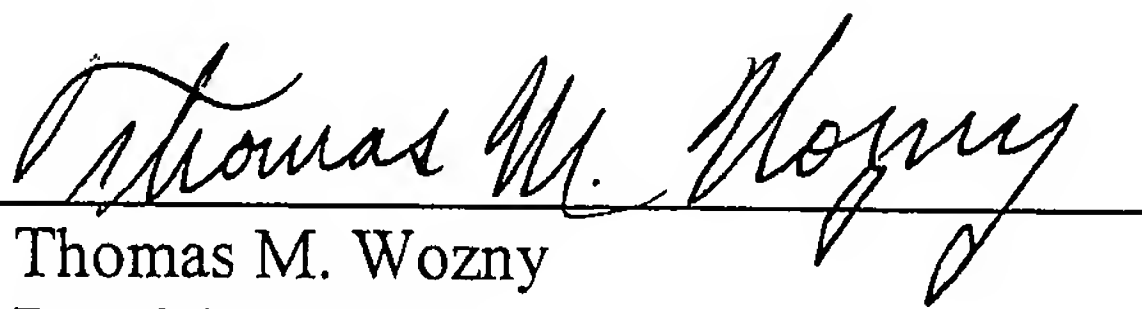
The Declaration will be forwarded promptly upon notification from the U.S. Patent and Trademark Office.

Please address all correspondence and telephone calls regarding this matter to:

Thomas M. Wozny
ANDRUS, SCEALES, STARKE & SAWALL, LLP
100 East Wisconsin Avenue, Suite 1100
Milwaukee, Wisconsin 53202
(414) 271-7590

Respectfully submitted,

ANDRUS, SCEALES, STARKE & SAWALL, LLP

By 
Thomas M. Wozny
Reg. No. 28,922

Andrus, Sceales, Starke & Sawall, LLP
100 East Wisconsin Avenue, Suite 1100
Milwaukee, WI 53202
(414) 271-7590

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of:

Keith R. Minnich

Mark C. Nicholson

RamKumar Karlapudi

Richard M. Schoen

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International Appl. No.

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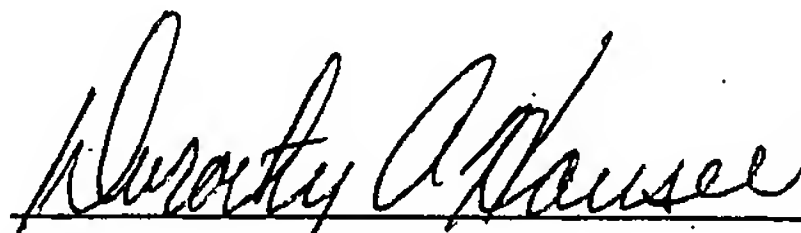
Priority Date Claimed:

26 November 2003

Method for Production of High Pressure
Steam from Produced Water

Attorney Docket No. 4553-00025

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PRELIMINARY AMENDMENT

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Sir:

In the matter of the above-identified patent application, please enter the following:

Amendments to the Specification begin on page 2 of this paper.

There are no Amendments to the Claims made in this paper, however, a listing of the claims begins on page 3 of this paper.

There are no Amendments to the Drawings made in this paper.

Remarks begin on page 7 of this paper.

In the Specification:

Please add the following heading and paragraph at page 1, between the title and the first line of text as follows:

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is the U.S. national stage application of International Application PCT/US2004/039515, filed 24 November 2004, which international application was published on June 16, 2005, as International Publication No. WO 2005/054746 in the English language. The International Application claims priority of United States Provisional Application No 60/525,578 filed on 26 November 2003.

Please add the enclosed "Abstract of the Disclosure" as new page 38 to the specification.

In the Claims:

1. (Original) A process for generating steam for downhole injection in a steam flood process for oil recovery, said process comprising:

(a) heating a de-oiled produced water stream containing water, dissolved solutes, and dissolved gases, said dissolved solutes further comprising at least one molecular species which is at low ionization levels when in solution at around neutral pH,

(b) raising the pH of said heated, produced water stream to maintain the solubility of said molecular species therein at a selected concentration factor,

(c) pressurizing and directing said produced water stream to a circulating concentrated brine in a produced water evaporator, said evaporator having a plurality of heat transfer surfaces,

(d) distributing said circulating brine across a first surface of at least one of said plurality of heat transfer surfaces to generate a steam vapor suitable for injection into a selected geological formation to fluidize oil,

(e) discharging at least some of said brine as an evaporator blowdown stream,

(f) distributing steam from a watertube boiler across a second surface of at least one of said plurality of heat transfer surfaces to condense said steam as a condensate,

(g) returning said condensate to said watertube boiler for steam production, and,

(h) discharging at least some of said condensate as a boiler blowdown to the produced water evaporator.

2. (Original) The process as set forth in claim 1, wherein said dissolved solutes further comprise hardness cations in a quantity that produces a scale deposition on said first surface of said heat transfer surfaces at said selected concentration factor.

3. (Original) The process as set forth in claim 1, wherein said produced water stream further comprises at least some non-hydroxide alkalinity.

4. (Original) The process as set forth in claim 1, wherein the pH is raised to between 10 and 11 and maintained in said evaporator circulating brine.

5. (Original) The process as set forth in claim 1, wherein the pH is raised to between 11 and 12 and maintained in said evaporator circulating brine.

6. (Original) The process as set forth in claim 1, wherein the pH is raised to between 12 and 13 and maintained in said evaporator circulating brine.

7. (Original) The process as set forth in claim 1, wherein the pH is raised to greater than or at least about 13 and maintained in said evaporator circulating brine.

8. (Original) The process according to claim 1, wherein the step of raising the pH is accomplished by addition of an inorganic base in aqueous solution, said base selected from the group consisting of sodium hydroxide, and potassium hydroxide.

9. (Original) The process as set forth in claim 3, wherein a portion or substantially all non-hydroxide alkalinity in said produced water stream is removed.

10. (Original) The process as set forth in claim 9, wherein the step of removing said non-hydroxide alkalinity, is further comprised of lowering the pH of said produced water stream to release at least some free carbon dioxide.

11. (Original) The process as set forth in claim 10, wherein the step of adjusting pH is accomplished by the addition of hydrochloric acid or sulfuric acid.

12. (Original) The process according to claim 1, wherein said produced water evaporator comprises a falling thin film evaporator, operating as a single unit, or operating in parallel, to generate said steam and said blowdown stream.

13. (Original) The process according to claim 1, wherein said produced water evaporator comprises a rising film or thermo-siphon evaporator, operating as a single unit, or operating in parallel, to generate said steam and said blowdown stream.

14. (Original) The method according to claim 1, wherein said heat transfer surfaces are tubular.

15. (Original) The method as set forth in claim 14, wherein said heat transfer surfaces are operated in a vertical position.

16. (Original) The method as set forth in claim 14, wherein said heat transfer surfaces are operated in a horizontal position.

17. (Original) The method as set forth in claim 14, wherein said heat transfer surfaces are designed for enhanced heat transfer.

18. (Original) The process according to claim 1, wherein said produced water evaporator comprises falling film and rising film in a combined process, operating as a single unit, or operating in parallel, to generate said steam and said blowdown stream.

19. (Original) The process as set forth in claim 14 wherein said circulating brine is heated on the interior of the tubes.

20. (Original) The process as set forth in claim 14 wherein said circulating brine is heated on the exterior of the tubes.

21. (Original) The process as set forth in claim 1, further comprising distributing said circulating brine across a first heat transfer surface of at least one of said plurality of heat transfer tubes to generate a steam vapor.

22. (Original) The process as set forth in claim 21, further comprising collecting said steam vapor and directing it to an injection well present in a selected geological formation, to produce an oil and water mixture.

23. (Original) The process as set forth in claim 21, wherein said steam vapor generated is at a pressure ranging from 200 to 1600 psig.

24. (Original) The process as set forth in claim 1, further comprising the step of treating said produced water evaporator blowdown stream in a zero liquid discharge process.

25. (Original) The process as set forth in claim 1, further comprising the step of injecting said produced water evaporator blowdown stream in a deep well for disposal.

26. (Original) The process as set forth in claim 24, wherein said zero liquid discharge comprises a steam driven multiple effect concentration and crystallization evaporator process to generate (a) high quality steam vapor and, (b) a high solute, high suspended solids slurry.

27. (Original) The process as set forth in claim 1, further comprising supplying said water tube boiler with de-ionized makeup water to produce said steam and a high solute containing blowdown stream.

28. (Original) The process as set forth in claim 27, wherein said de-ionized makeup water is produced by a reverse osmosis unit.

29. (Original) The process as set forth in claim 26, further comprising, dewatering said generated suspended solids slurry in a filter press or belt filter and, further comprising, recycling the filtrate back to the crystallization effect of the multiple effect evaporator.

30. (Original) The process as set forth in claim 24, wherein said zero liquid discharge comprises a steam driven crystallizer evaporator process to generate (a) high quality steam vapor and, (b) a high solute, high suspended solids slurry, and, further comprising, dewatering said generated suspended solids slurry in a filter press or belt filter and, further comprising, recycling the filtrate back to the inlet of the crystallizer evaporator.

31. (Original) The process as set forth in claim 27, wherein said de-ionized makeup water is produced by an ion exchange unit.

32. (Original) The process as set forth in claim 28 or claim 31, wherein the feed water utilized for de-ionized makeup water is fresh water.

33. (Original) The process as set forth in claim 2, wherein a portion or substantially all hardness cations are removed in a deionization zone.

34. (Original) The process as set forth in claim 1, wherein said molecular species is silica.

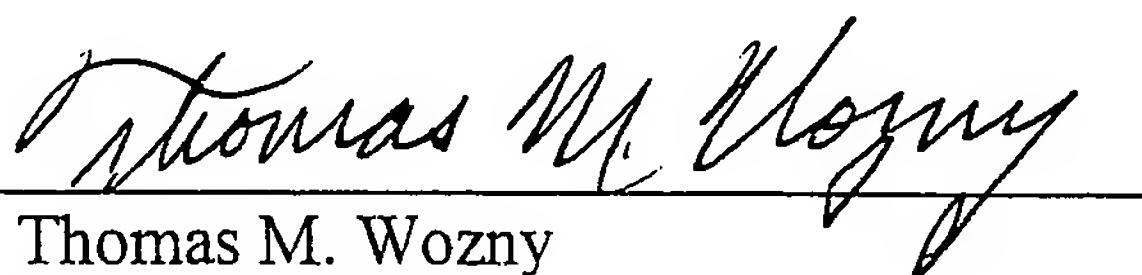
REMARKS

The present Preliminary Amendment is being filed in order to provide an Abstract of the Disclosure as new page 38 of the specification and make of record the claim to priority.

Applicant believes the application is in condition for examination and respectfully requests same.

Respectfully submitted,

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METHOD FOR PRODUCTION OF HIGH PRESSURE STEAM FROM PRODUCED WATER

ABSTRACT

5 An evaporation based method for generation of high pressure steam from
produced water in the heavy oil production industry. De-oiled produced water is
processed through a high pH/high pressure evaporator driven by a commercial
watertube boiler. The vapor produced by the evaporator is suitable for the steam
assisted gravity drainage (SAGD) method being utilized by heavy oil recovery
installations, without the use of once through steam generators that require
10 extensive chemical treatment, and without requiring atmospheric distillation, which
requires high power consuming compressors. Evaporator blowdown may be
further treated in a crystallizing evaporator to provide a zero liquid discharge
(ZLD) system and, with most produced waters, at least 98% of the incoming
produced water stream can be recovered in the form of high pressure steam.

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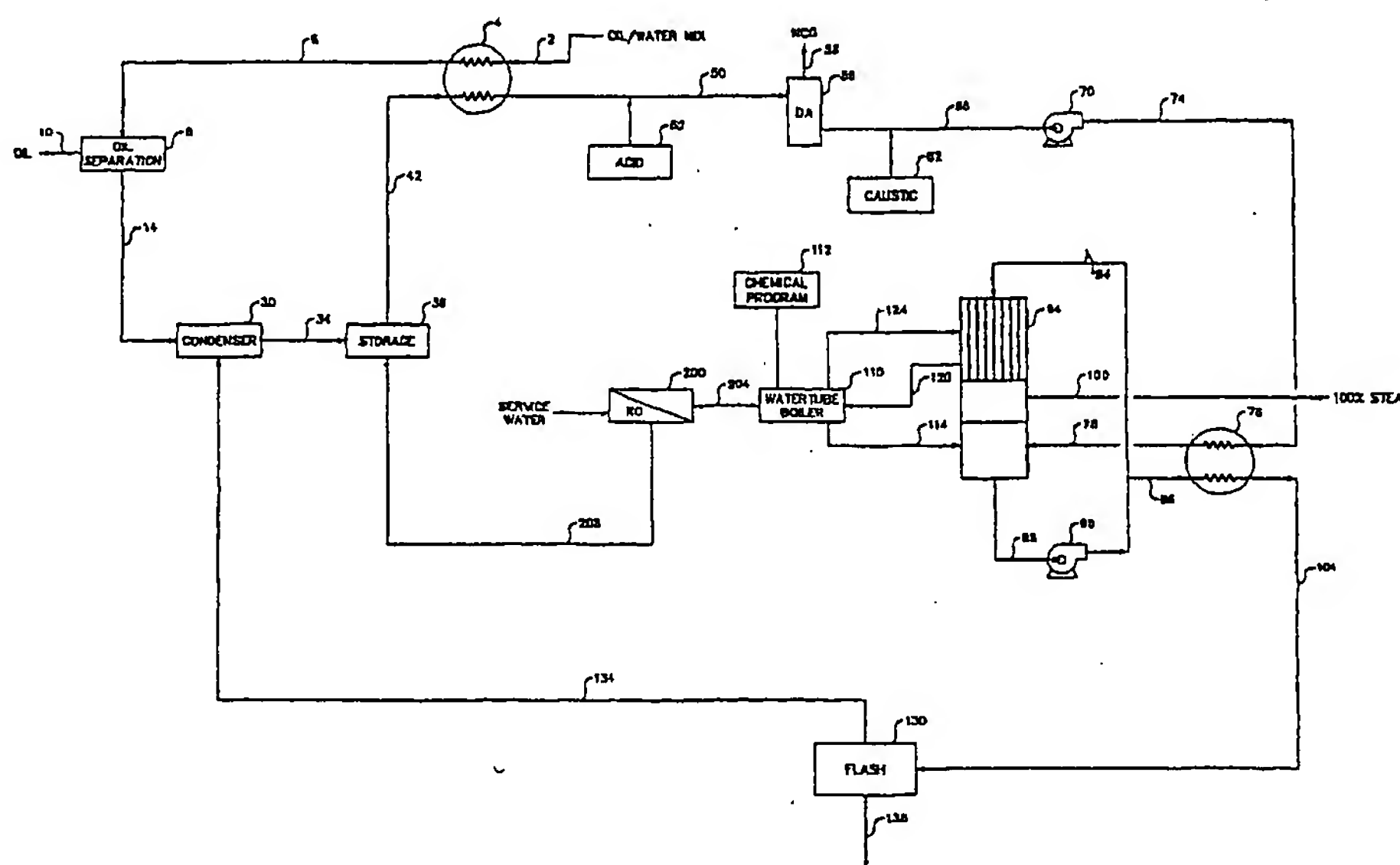
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[Continued on next page]

(54) Title: METHOD FOR PRODUCTION OF HIGH PRESSURE STEAM FROM PRODUCED WATER



(57) Abstract: An evaporation based method for generation of high pressure steam from produced water in the heavy oil production industry. De-oiled produced water is processed through a high pH/high pressure evaporator (84) driven by a commercial watertube boiler (110). The vapor produced by the evaporator is suitable for the steam assisted gravity drainage (SAGD) method being utilized by heavy oil recovery installations, without the use of once through steam generators that require extensive chemical treatment, and without requiring atmospheric distillation, which requires high power consuming compressors. Evaporator blowdown may be further treated in a crystallizing evaporator to provide a zero liquid discharge (ZLD) system and, with most produced waters, at least 98% of the incoming produced water stream can be recovered in the form of high pressure steam.

WO 2005/054746 A3



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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 F22B E21B C02F F01K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2003/127226 A1 (HEINS WILLIAM F) 10 July 2003 (2003-07-10) paragraphs '0014! - '0025!, '0043! - '0056!; figures 4,5 abstract	1-34
A,P	US 6 733 636 B1 (HEINS WILLIAM F) 11 May 2004 (2004-05-11) column 4, line 17 - column 6, line 67; figures abstract	1-34
A	US 4 418 651 A (WYATT ET AL) 6 December 1983 (1983-12-06) column 5, line 22 - column 7, line 5; figures 1,4 abstract	1-34
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 730 577 A (HOUGHTON ET AL) 15 March 1988 (1988-03-15) column 2, line 19 - line 51 column 2, line 63 - column 3, line 55; figure abstract	1-34
P,A	----- US 6 675 747 B1 (GOIDICH STEPHEN J ET AL) 13 January 2004 (2004-01-13) the whole document -----	1-34

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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			US 2005022989 A1	03-02-2005
			CA 2307819 A1	07-11-2000

US 6733636	B1	11-05-2004	US 2003127226 A1	10-07-2003
			US 2005022989 A1	03-02-2005
			CA 2307819 A1	07-11-2000

US 4418651	A	06-12-1983	NONE	

US 4730577	A	15-03-1988	NONE	

US 6675747	B1	13-01-2004	CA 2437479 A1	22-02-2004
			CN 1485568 A	31-03-2004



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METHOD FOR PRODUCTION OF HIGH PRESSURE STEAM FROM PRODUCED WATER

TECHNICAL FIELD

[0001] This process relates generally to a method and to a water evaporation system for the treatment of produced waters and high quality steam generation for operations that utilize high-pressure steam to recover oil from geological formations.

BACKGROUND OF THE INVENTION

[0002] Oil producers utilize different means to produce steam for injection into the oil bearing formation. The steam that is injected into the geologic formation condenses by direct contact heat exchange, thus heating the oil and reducing its viscosity. The condensed steam and oil are collected in the producing well and pumped to the surface. This oil/water mixture, once the oil has been separated from it, is what is referred to as 'produced water' in the oil industry.

[0003] Since water can comprise up to 90% of every barrel of oil/water mixture removed from the formation, the recovery and reuse of the water is necessary to control the cost of the operation and to minimize the environmental impact of consuming raw fresh water and subsequently generating wastewater for disposal. Once the decision to recover water is made, then treatment of those produced waters is required to reduce the scaling and/or organic fouling tendency of the water. This treatment generally requires the removal of the hardness and other ions present in the stream, preferably to near zero. As is understood in the art, the 'hardness' causing ions are the combined calcium and magnesium salts in the water to be used in steam generation equipment and is typically expressed as parts per million (ppm) although other terms can be used. While silica is not considered as adding to the hardness value, its presence can also lead to scaling problems if present in other than minimal amounts.

[0004] The traditional method for generation of steam in enhanced oil recovery is to utilize a once-through steam generator (OTSG) in which steam is

generated from a treated feedwater through tubes heated by gas or oil burners. The OTSG feedwater can have a total dissolved solids concentration as high as 12,000 ppm (as CaCO₃ equivalent), but requires a hardness level that is near zero. This method produces a low quality or wet steam, which is 80% vapor and 20% liquid, at pressures ranging from 600 pounds per square inch gauge (psig) up to 2000 psig. This 80% quality steam is separated from the 20% water and then injected into the formation. Either a portion or all of the 20% blowdown is disposed as a wastewater. Another method that has been proposed to obtain the high quality steam requirement is using a water tube boiler instead of the OTSG to generate steam. The water tube boiler, however, requires an even greater amount of feedwater pretreatment than the OTSG to ensure problem free operation. For a comparison of the feedwater requirements for both OTSG and water tube boilers, refer to Figures 6 and 7. There are numerous ways to obtain the feedwater quality required for steam generation, several of which are outlined below for illustration.

[0005] The oil/water mixture coming out of the production well is sent to the primary oil-water separator where substantially all of the oil is separated from the produced water. This separator can be comprised of any known apparatus, but typically, it is comprised of one or more free-water-knock-outs (FWKO), which allow separation of the oil and water by gravity. The separated oil is further treated to remove the last of the water and then sent to storage.

[0006] The separated produced water is sent to a cone bottom tank where heavy solids, such as sand, are allowed to settle out and any remaining oil rises to the top for removal. If any substantial oil remains after this step, one or more induced gas flotation units are utilized to remove substantially all of the oil present in the produced water. Alternately, a de-oiling polymer can be used with a resultant waste oil/solids sludge, which needs further handling for disposal.

[0007] The de-oiled produced water stream is then further treated for reuse. Its constituents are variable but typically it is relatively high in total dissolved solids (TDS), total organic carbon (TOC), hardness, and silica. The water

treatment plant schemes which have heretofore been utilized downstream of the de-oiling zone and upstream of the steam injection well, as well as the equipment which is necessary or desirable to obtain high quality steam at 600 psig, or greater, is the focus of the improvements explained and described in this disclosure.

[0008] Referring to Figure 1, which outlines a typical prior art process used to obtain high quality steam for down hole injection, the raw produced water 6 is sent to a de-oiling process zone 8 and then to a warm lime softener 310. Chemicals 312 such as $\text{Ca}(\text{OH})_2$, Na_2CO_3 , MgO , NaOH , and a coagulant are introduced into the lime softener depending on the reaction desired and a precipitate consisting of hardness and silica is generated. Following the lime softener, a media type filter 324 is utilized to remove the small suspended solids that were not caught up in the lime sludge. The partially softened produced water, still saturated in calcium (as CaCO_3), is then further de-ionized in a weak acid cation (WAC) exchanger 18 which essentially removes all remaining divalent ions. The softened produced water is then sent to the once through steam generator 230, via a conduit that passes through pre-heaters (4 and 76), and 80% quality steam 236 is generated. A steam separator 240 removes the 20% water entrainment and produces high quality steam 100 for down-hole injection in the steam flooding process. The high temperature blowdown 96 from the steam separator is then sent to a series of flash tanks to provide progressively lower steam pressures for other uses. If zero liquid discharge is desired, then the flash steam 134 can be used in a steam driven multiple effect evaporator and crystallizer 140 to obtain a zero liquid discharge (ZLD) system.

[0009] This prior art method is known technology and is considered to be the industry standard. However, it carries with it several disadvantages. These are:

[0010] 1. It has the highest chemical cost of any options

[0011] 2. It has the highest cost for sludge and salt cake disposal requirements

[0012] 3. The OTSG's are limited by the 80% conversion of water into steam

- [0013] 4. The OTSG has inherent design problems in terms of tube wetting, fouling, and scaling
- [0014] 5. In cold weather operations, the sludge from the lime softener becomes very hard to handle
- [0015] 6. In the event of an unscheduled maintenance shutdown, the sludge in the lime softener can quickly set up in a form similar to concrete and become very hard to remove from the system.
- [0016] Figure 2 depicts another current prior art process in which the lime soda softening, media filter, and polishing WAC are replaced by a mechanical vapor compressor evaporator (MVC) 244. The de-oiled produced water 14 may be treated with an acid such as hydrochloric (HCl) to lower the pH and destroy any non-hydroxide alkalinity present. Any non-condensable gasses (NCG) 58 present may be removed in deaerator 56. Caustic such as sodium hydroxide (NaOH) 62 may then be added to raise the pH to around 10 or higher. The MVC evaporator 244 produces a low TDS distillate stream 246 that is used to feed the OTSG 230 and the process of generating high pressure steam for down-hole injection is accomplished in the same manner as in Figure 1. In this case, the blowdown 96 from the steam separator 240 is flashed to a steam driven crystallizer 252 which concentrates the brine blowdown 248 from the MVC evaporator 244 and thus provides a ZLD system. The low TDS vapor produced in crystallizer 162 is routed through conduit 166, where it is combined with the liquid portion 138 exiting the flash tank 130, and then to the OTSG feed storage tank 36.
- [0017] While this process seems to provide a simple approach to providing high quality water to the OTSG, it has limited applicability in that the concentration of the hardness causing ions, such as calcium and magnesium, must be quite low in the raw produced water. If the hardness ions are not low, then the MVC is limited in the concentration factor obtainable, scale control chemicals are required, or it has to operate in the seeded-slurry mode to avoid calcium sulfate and silica scaling. In the seeded-slurry mode, calcium chloride (CaCl_2) and/or sodium sulfate (Na_2SO_4)

has to be added to the feed stream to ensure that a circulating magma of calcium sulfate (CaSO_4) crystals, typically 3-10% suspended solids (SS), is maintained in the MVC evaporator 244. This circulating magma is used as precipitation sites for the incoming calcium ions and for the co-precipitation of silica. This seeded-slurry mode of operation is aptly taught in U.S. Patent No. 4,618,429.

[0018] The disadvantages to this system are:

[0019] 1. Power consumption is high due to MVC evaporator compressor

[0020] 2. A very large electrical infrastructure is required to supply power to the MVC evaporator compressors

[0021] 3. Suppliers of OTSG equipment are reluctant to design to greater than 80% quality steam even with high quality feed water

[0022] 4. OTSG tube wetting problems

[0023] 5. Applicability is limited to low calcium and low magnesium produced waters due to high pH requirements for silica solubility and even when low, acid cleanings are required to maintain evaporator efficiency by removing the CaCO_3 scale that builds up.

[0024] 6. The evaporator is subject to scaling from low solubility constituents in the evaporator feed like strontium, barium and complexes of metals that occur at high pH operation.

[0025] Figure 3 is yet another prior art process that utilizes a MVC evaporator 244 to pre-treat the de-oiled produced water in the same manner as that shown in Figure 2. In this case though, the high quality distillate 246 from the MVC 244 is cooled in heat exchanger 280 and sent via conduit 284 to a reverse osmosis unit (RO) 290 that removes the volatile TOC from it. The RO permeate 294 is then suitable for use by a high efficiency water tube boiler 110 that will produce high quality steam. The need for a steam separator system and blowdown condensate system is eliminated. Likewise, the inherent problems of an OTSG are thus eliminated and a greater conversion of water to steam is obtained. The

blowdown from the boiler is directed to the MVC (262). The steam driven ZLD system of the preceding figures has to be eliminated in favor of a MVC driven system as the amount of blowdown from the water tube boiler is insufficient to support a steam driven evaporator. Due to compressor limitations, an MVC crystallizer 268 is also required for final concentration. On some produced waters, notably those with minimal non-volatile TOC, the RO system 290 is not required and the MVC distillate 246 is directed to the watertube boiler 110 without any further treatment. However, this variation has the potential of fouling and scaling the watertube boiler to a greater extent than when distillate post treatment is utilized.

[0026] The advantages of this system are the incorporation of the water tube boiler and a lower operating cost, due to lower fuel consumption, as compared to the MVC/OTSG Figure 2 process.

[0027] The disadvantages of this system include:

[0028] 1. Highest power consumption and highest electrical infrastructure requirements

[0029] 2. High total cost compared to other options

[0030] 3. Multiple types of MVC evaporators are required (pretreatment/blowdown and crystallizer) which complicates operation

[0031] 4. TOC is all rejected to the pretreatment/blowdown and crystallizer MVCs which will likely cause foaming problems that will complicate operation and puts the MVC compressors at risk of damage

[0032] 5. Pretreatment MVC evaporator distillate must be cooled prior to RO treatment and then reheated.

[0033] In summary, the prior art process designs in current use for treating heavy oilfield produced waters for high quality steam generation to be utilized in down-hole steam flooding applications is not entirely satisfactory due to:

[0034] 1. physical chemical treatment processes are usually extensive, require high maintenance and operator interface, and generate large sludge

and regeneration streams that need to be dealt with in accordance with strict environmental regulations,

[0035] 2. large quantities required of expensive treatment chemicals that, in cases, need special safety/handling procedures,

[0036] 3. reliance on low efficiency OTSGs to generate high quality steam at a recovery rate of 80%, water to steam and the associated steam separator and blowdown condensate handling systems,

[0037] 4. inherent OTSG problems with insufficient tube wetting, high heat transfer rates, and tube plugging,

[0038] 5. high power consumption requirements and electrical infrastructure due to the use of vapor compressors,

[0039] 6. treating the entire produced water stream to meet requirements for ASME grade water that can be utilized in a commercial water tube boiler.

[0040] As water is becoming increasingly expensive to treat, or in short supply, or both, it would be desirable to simplify the treatment necessary to generate high quality, high pressure steam and reduce the costs. Finally, it would be clearly desirable to meet such increasingly difficult water treatment objectives with better system availability and longer run times than is commonly achieved today.

[0041] It is believed that no one heretofore has thought it feasible to operate a water tube boiler on deionized water coupled to an evaporator system at high pH and at pressures high enough to provide steam that can be directly used for steam flooding projects. The conventional engineering approach has been to design systems such as those depicted in the prior art Figures 1-3 or to limit the final concentrations to levels that do not cause scaling problems.

[0042] Therefore, a heretofore unaddressed need exists in the heavy oil industry to address the aforementioned deficiencies and inadequacies. Accordingly, it would be advantageous to address the drawbacks to current practice, which

would help both the environment and assist the production facility ownership and operations area in controlling costs.

SUMMARY OF THE INVENTION

[0043] The present invention provides a novel high pressure steam generation method for produced water employing industrial high TDS brine concentration technology that eliminates the need for once through steam generators and power consuming vapor compressors.

[0044] In a unique process for producing high pressure steam vapor, de-oiled produced waters of low hardness and low non-hydroxide alkalinity are injected with a caustic solution to raise the pH prior to high pressure steam generation (HiPVap). In situations wherein scale causing non-hydroxide alkalinity is present in the produced water feed stream, an acid injection system is used to destroy the alkalinity prior to raising the pH for steam generation in the HiPVap.

[0045] The preferred design used in the present invention provides a produced water steam generation plant that overcomes a number of important and serious problems. First, the use of problem prone low efficiency once through steam generators for high pressure steam production is no longer required. Second, the pretreatment requirements of the produced water, prior to high pressure steam generation, are minimized or eliminated entirely. Sludge streams associated with warm lime softening are eliminated. Third, the process as disclosed herein, is completely steam driven and there is no requirement for high energy consuming mechanical vapor compressors or electrical infrastructure. Fourth, controlled levels of multivalent cations, combined with controlled levels of non-hydroxide alkalinity, substantially eliminates the precipitation of scale forming compounds associated with sulfate, carbonate, or silicate anions. Thus, cleaning requirements are minimized. This is important commercially because it enables a water treatment plant to avoid lost water production, which would otherwise undesirably require increased treatment plant size to accommodate for the lost production during

cleaning cycles. Fifth, the preferred high pH operational conditions enable a high degree of ionization to be achieved in various species which are sparingly ionized at neutral or near neutral pH in aqueous solution, such as silica, to enable such species to be concentrated to higher levels before precipitation. Sixth, another benefit to HiPVap operation is the use of industry accepted water tube boilers, the feed to which is not organic laden makeup water. Finally, the HiPVap steam generation process has the benefits of a very high brine recirculation rate to evaporation rate ratio, which results in better heat transfer surface wetting, and a lower temperature difference combined with a lower heat transfer rate across the heat transfer surface than an OTSG operating on the same produced water. The result is a better design with less scaling potential and higher allowable concentration factors.

[0046] OBJECTS, ADVANTAGES, AND NOVEL FEATURES

[0047] A new process for producing high-pressure high quality steam from produced water disclosed herein, and various embodiments thereof, can be applied to the heavy oil industry. Such embodiments are particularly advantageous in that they consume less electrical power, minimize the generation of waste products, utilize waste heat, minimize maintenance, and are superior to current water treatment processes heretofore used in the recovery of oil from tar sands and other heavy oil operations.

[0048] From the abovementioned, it will be observed that one of the significant and major objectives resides in the provision of a novel process, including variations thereof, for the treatment of produced waters, so that such waters can be recovered and re-used in producing steam for use in heavy oil recovery operations.

[0049] Another important objective is to simplify process plant flow sheets by minimizing the number of unit processes required in water treatment trains, which simplifies operations and lowers costs in heavy oil recovery operations.

[0050] Other important, but more specific objectives reside in the provision of various embodiments of an improved water treatment process for production of high quality steam for down-hole use in heavy oil recovery, which:

[0051] (a) eliminates the requirement for once through steam generators and separation of high pressure steam from residual hot condensates;

[0052] (b) eliminates the generation of softener sludges;

[0053] (c) reduces electrical power consumption by utilizing steam as the energy source instead of mechanical vapor compressors;

[0054] (d) minimizes operation and maintenance labor requirements;

[0055] (e) reduces the capital and operating costs of water treatment equipment; and

[0056] (f) minimizes chemical additives and associated handling requirements.

[0057] Other important objects, features, and additional advantages of the invention will become apparent to those skilled in the art from the foregoing and from the appended claims, in conjunction with the detailed discussion below and the accompanying drawing.

[0058] BRIEF DESCRIPTION OF THE DRAWINGS

[0059] In the drawings:

[0060] For comparative purposes, all of the prior art examples shown herein incorporate the Zero Liquid Discharge (ZLD) concept as a part of the illustration although, in many current installations, waste disposal is accomplished by deep-well injection. Those skilled in the art will recognize that merely minimizing the blowdown stream without the use of a dewatering device may, on certain occasions, also qualify the system as ZLD. The high pressure, high efficiency evaporation method defined herein is site specific wherein individual process steps are customized to fit the specific feed water, and needs of the customer. For that reason, all possible embodiments of this novel method of water treatment are not

illustrated and, as those skilled in the art can appreciate, other illustrative embodiments would merely reflect variations and rearrangement of some components without affecting the spirit or concept of this invention.

[0061] The same identifier will reference identical features depicted in each of the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0062] In the drawings:

[0063] FIG. 1 is a schematic diagram that shows a prior art process, specifically a generalized process flow diagram for one typical physical-chemical water treatment process used in steam assisted gravity drainage (SAGD) heavy oil recovery operations.

[0064] FIG. 2 is a schematic diagram that shows a prior art process, specifically a generalized process flow diagram wherein the physical-chemical water treatment method is replaced by a mechanical vapor compression (MVC) process to supply purified water to a once through steam generator (OTSG) used in steam assisted gravity drainage (SAGD) heavy oil recovery operations.

[0065] FIG. 3 is a schematic diagram that illustrates a prior art process in which the distillate from a mechanical vapor compression (MVC) method is further treated in reverse osmosis (RO) equipment that enables replacing a once through steam generator (OTSG) with a commercial packaged boiler in steam assisted gravity drainage (SAGD) heavy oil recovery operations.

[0066] FIG. 4 is a schematic diagram that shows one embodiment of the novel steam generation process disclosed and claimed herein, illustrating the use of the process for high pressure steam production with produced waters low in hardness and alkalinity in steam assisted gravity drainage (SAGD) heavy oil recovery operations.

[0067] Fig. 5 is a schematic diagram that illustrates another embodiment of the novel steam generation process disclosed and claimed herein, illustrating the

use of the HiPVap process on produced waters classified as high in hardness and carbonate alkalinity ions.

[0068] FIG. 6 is a table that shows the typical feedwater quality requirements for steam generators which produce steam in the 1000 pounds per square inch gauge (PSIG), or thereabouts, for once through steam generator installations.

[0069] FIG. 7 is a table that shows the typical feedwater quality requirements for watertube boilers which produce steam in the 1000 pounds per square inch gauge (PSIG), or thereabouts, for watertube boiler installations.

[0070] FIG. 8 is a graph that details the ionization of silica as a function of pH.

[0071] The foregoing figures, being merely exemplary, contain various elements that may be present or omitted from actual process implementations depending upon the circumstances. An attempt has been made to draw the figures in a way that illustrates at least those elements that are significant for an understanding of the various embodiments and aspects of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0072] Heavy oil recovery operations have increasingly incorporated the steam assisted gravity drainage (SAGD) method to recover oil from tar sand and other networks. In this method the injected steam is more efficiently utilized as 100% quality (i.e., no liquid water entrained with the steam) in contrast to older methods in which an 80% steam/20% water mixture was used for steam flooding of the oil field. However, the once through steam generators (OTSG) in standard use are designed to generate 80% quality steam which then requires the use of steam separators to remove the entrained water portion to provide 100% quality steam for down-hole injection. The use of an OTSG to supply the 100% quality steam required for steam flooding leaves the high pressure high temperature liquid portion that needs to be handled and disposed of. In some cases it can be utilized for other steam consumers by using a sequential arrangement of flash tanks, each providing a

lower pressure steam, but ultimately resulting in a liquid stream that had to be disposed of.

[0073] Heavy oil recovery operators are now looking at commercial water tube boilers to generate the 100% steam quality required. This became the desired next step since water tube boilers are designed to provide high purity steam at the pressures required for steam flooding, whereas the installation, operating, and maintenance expenses are lower than OTSGs, and the high efficiency of the water tube boiler results in a small blowdown stream that requires disposal. However, the use of a water tube boiler required a more extensive water pretreatment process as the feedwater requirements are much stricter than for an OTSG. Refer to FIG. 6 and FIG.7 for a comparison of the feedwater characteristics required for the water tube boiler installation in comparison to the OTSG. The industry recognizes that the only way to achieve the water quality required for water tube boilers is to remove the dissolved solutes and TOC (Total Organic Carbon) present in produced waters. This level of pre-treatment requires membrane separation and/or evaporative process. Cooling and subsequent reheating of the produced water are required for membrane systems due to their temperature limitations. Also, the evaporation processes that have been considered (reference Figures 2 and 3) are energy intensive.

[0074] The invention disclosed herein provides a novel integrated process for generating high pressure steam from produced water. The energy that would normally only be used once to generate injection steam is used twice in this process. The first use of the energy is the generation of steam from high purity water in a water tube boiler. The second use is the generation of injection steam from produced water. The generation of injection steam from produced water is accomplished by utilizing a high pressure, high efficiency HiPVap process. This overcomes the disadvantages of the low efficiency OTSG, the requirements for treating the full produced water feed stream to ASME quality standards for water tube boilers, and high power consumption by the MVC installations. When

incorporated with the zero liquid discharge (ZLD) in one embodiment, recoveries greater than 98% of the produced water feed stream are attainable at a cost effective price with no liquid streams requiring disposal.

[0075] Present day state of the art steam generation, either OTSG or watertube boiler, is limited on how much water can be recovered by scale causing ions, such as hardness and silica, which are inherent in these waste streams, total organic carbon (TOC), and maximum total dissolved solids (TDS) allowable in the feed stream. The additions of expensive scale inhibiting agents or scale control methods are beneficial but still have their limits of usefulness. Evaporators that are used as industrial brine concentrators overcome the TDS limitations with their built in high solids capability and heat transfer surface wetting design. They can also handle high TOC loadings but volatile TOC carries over with the generated vapor which, when condensed, passes into any downstream users of the distillate produced causing scaling and/or fouling problems.

[0076] The present invention provides a novel process to overcome these limitations and recover more of the produced water for steam generation than was previously possible by providing a high pH scale free environment in a high pressure, high efficiency HiPVap process that incorporates the high solutes capability of industrial brine concentrators. Volatile TOC does not present a problem as it is carried out with the high pressure steam vapor and sent to the borehole for steam injection. In addition, the HiPVap process does not require any additional energy to produce high pressure injection steam, as compared to conventional OTSG systems, and uses significantly less energy than the current MVC evaporative technologies.

[0077] Although it may seem impractical to use steam to generate steam, the practice has positive benefits when applied as disclosed herein. Of prime importance is the fact that both the industrial high pressure evaporator and the watertube boiler are being operated in the environments that they were originally designed for; i.e. a high TDS brine concentrating evaporator coupled with a high

pressure high purity ASME grade watertube boiler. This leads to equipment reliability and reduced costs. The cost reductions can be broken down into lower operating costs, since there is no requirement for mechanical vapor compressors, and lower water pretreatment capital costs, since there is not a requirement for extensive water conditioning associated with changing a produced water into ASME quality water.

[0078] Attributes that characterize the high pressure, high efficiency evaporator (HiPVap) process design and operation are:

[0079] Generation of high quality steam at pressures ranging from 200 to 1600 psig without the use of a low efficiency once through steam generator (OTSG).

[0080] The ratio of evaporation to recirculation of produced water inside the HiPVap unit is very low, thus the heat transfer surface stays very well wetted and scaling potential along with dry spots is minimized.

[0081] Lower power consumption and lower electrical infrastructure costs as electrically driven steam vapor compressors are not required.

[0082] Time proven conservative industrial design for the evaporation of high TDS streams with high organic levels.

[0083] Elimination of lime softening waste streams which are difficult to handle in cold climates.

[0084] Simplified pretreatment process for de-oiled produced water prior to steam generation.

[0085] Very high solubility of weak acid anions such as silica when operating at a high pH.

[0086] Very high achievable concentration factors (recovery--ninety percent (90%) or higher recovery can be achieved).

[0087] Cleaning frequency is substantially reduced.

[0088] Addition of scale inhibitors is virtually eliminated.

[0089] Corrosion potential is reduced by operation at high pH thus allowing the use of low cost materials of construction.

[0090] Reduced overall operating cost, compared to conventional produced water recovery and steam generation systems.

[0091] Reduced overall capital cost, compared to conventional produced water recovery and steam generation systems.

[0092] The HiPVap process is site-specific. Individual process steps are customized to fit the particular produced water at a given site. Regardless of the difference in the pretreatment process for different sites, one process parameter is common for all applications, namely that the HiPVap system is operated at the highest feasible blowdown pH. This factor enables the circulating solution to provide a low corrosion potential, high silica tolerant, and non-fouling organic environment at the heat transfer surface.

[0093] With reference to the various figures, produced water feed stream 14 will typically contain soluble and insoluble, organic and inorganic components. The inorganic components can be salts such as sodium chloride, sodium sulfate, calcium chloride, calcium carbonate, calcium phosphate, barium chloride, barium sulfate, and other like compounds. Metals such as copper, nickel, lead, zinc, arsenic, iron, cobalt, cadmium, strontium, magnesium, boron, chromium, and the like may also be included. Organic components are typically dissolved and emulsified hydrocarbons such as benzene, toluene, phenol, and the like.

[0094] Produced waters utilized for production of steam additionally include the presence of silicon dioxide (also known as silica or SiO_2) in one form or another, depending upon pH and the other species present in the water. For evaporator systems, scaling of the heat transfer surface with silica is to be avoided. This is because (a) silica forms a relatively hard scale that reduces productivity of the evaporator, (b) it is usually rather difficult to remove, (c) the scale removal process produces undesirable quantities of spent cleaning chemicals, and (d) cleaning cycles result in undesirable and unproductive off-line periods for the

equipment. Therefore, regardless of the level of silica in the incoming raw feed water, operation of conventional evaporation processes, without a scale control method such as preferential deposition seeded slurry, generally involves concentration of SiO_2 in the high solids stream to a level not appreciably in excess of 150 ppm of silica (as SiO_2). This requires that evaporator systems be operated at lowered concentration factors (recovery rates) to prevent silica concentration in the blowdown stream from exceeding solubility limits. Seeded slurry systems can be taken to concentration factors that surpass the solubility of silica but rely on seed management procedures and are still prone to scaling of the evaporator heat transfer surfaces.

[0095] It is commonly understood that the solubility of silica increases with increasing pH, and that silica is quite soluble in high pH aqueous solution. The increase in silica solubility is basically proportional to the change in ionization as increased ionization results in the soluble silicate ion being the dominant species. The solubility is not directly proportional because even un-dissociated silica exhibits some solubility in aqueous solutions, typically up to about one hundred twenty (120) ppm to one hundred sixty (160) ppm, depending upon temperature and other factors. In comparison, it has been demonstrated that silica solubility at pH 11 is in excess of one thousand five hundred (1,500) ppm at ambient temperature; silica is increasingly soluble as temperature and/or pH increases.

[0096] Silica is very weakly ionized when in neutral or near neutral aqueous solutions and is generally considered to exist as un-dissociated (meta/ortho-) silicic acid (H_4SiO_4) in most naturally occurring waters with a pH of up to about 8. The dissociation constant (pKa) value for the first stage of dissociation of silica has been reported at approximately 9.7, which indicates that silica is approximately fifty percent (50%) ionized at a pH of 9.7; the other fifty percent (50%) remains as un-dissociated (ortho) silicic acid at that pH. A graphical representation of the relationship between pH and the percent silica ionization is shown in FIG. 8. Clearly, it would be advantageous, where silica ionization is desired, to operate at a

pH in excess of 10, and more preferably, in excess of 11, and yet more preferably, in excess of 12 where the entire silica molecule is present as a soluble silicate ion.

[0097] Therefore, increasing the pH of the HiPVap process thus provides the major benefit of increased silica solubility. To gain maximum benefit from silica ionization at high pH, the HiPVap system should be operated at a pH as high as possible. Preferably, the evaporator system is operated at a pH of about 10.5 or above, and more preferably, at a pH of 11 or higher.

[0098] By maintaining hardness and non-hydroxide alkalinity at levels which effectively avoid formation of scale at a selected pH for HiPVap process, the concentration of SiO_2 in the HiPVap blowdown stream can be safely increased to at least 5500 ppm, or more. This is accomplished by raising the pH of the produced water fed to the HiPVap system and without the use of silica scale inhibition chemicals or control methods.

[0099] The novel process disclosed herein is situated between the oil separation zone, 8 in the various figures, and the steam injection well used for steam flooding in oil recovery installations. The separated and de-oiled produced water 14, typically with 10 to 20 ppm residual oil, is analyzed for calcium carbonate scale forming potential by use of scale indexes such as the Langelier Saturation Index, the Stiff-Davis Index, and other solubility tables. These indexes, as is known to those with ordinary skill in the art and to whom this specification is directed, take as input the calcium, magnesium, alkalinity, pH, and temperature of operation to determine what amount, if any, of the scale causing ions present in the produced water must be reduced for scale free operation. Other tables, based on calcium sulfate and silica, are also used to determine the solubility levels and concentration factors attainable with these compounds in the produced water stream. After determining the scaling potential of the produced water, an embodiment of this novel process is chosen that will ensure scale free operation at the concentration factor required.

[00100] Referring to FIG. 4 or FIG. 5, following any produced water conditioning, as determined by the appropriate indexes and solubility charts, the herein disclosed novel high pressure, high efficiency HiPVap 84 must be operated in such a manner that the pH of the blowdown is approximately, but preferably not higher than, 12.5. The selected pH is based on the amount of silica in the produced water feed stream along with the concentration factor required and may be lower, but not lower than 10.5, depending on site specific design conditions.

[00101] FIG. 4 represents the HiPVap process as it would be incorporated into a SAGD application with typical produced water containing low hardness and low alkalinity solutes. The necessary pretreatment and conditioning prior to the HiPVap process is accomplished by the addition of acid 52, such as sulfuric or hydrochloric, when necessary and or appropriate, to lower the pH sufficiently to convert bound carbonate alkalinity to gaseous carbon dioxide. The carbon dioxide along with other non-condensable gasses (NCG) such as oxygen and nitrogen are then removed in the HiPVap deaerator 56. Following the deaerator 56, the produced water feed stream is then conditioned by the addition of caustic 62, such as sodium hydroxide or potassium hydroxide, to a pre-selected pH prior to the HiPVap 84 process.

[00102] In the HiPVap 84, the treated and conditioned produced water 78 mixes with and dilutes the concentrated high solids stream present in line 88. This stream is recirculated with high pressure recirculation pump 90 and a small portion is removed as HiPVap blowdown through line 96 on each pass through the HiPVap 84. The solutes in the produced feed water are concentrated in HiPVap 84 by removing water from the diluted recirculating solution in line 94 as it passes over the heat transfer surface. As depicted in Figure 4, the HiPVap utilizes falling thin film evaporation wherein the recirculated stream depicted by line 94 is thinly spread across the inner, or first, surface of a plurality of heat transfer tubes. A small portion of water is removed from the thin recirculating stream in the form of steam vapor driven by the high pressure steam in line 124 which is condensing on

the outside of the heat transfer tubes. The water that has been removed, in the form of high temperature steam at the high pressures necessary for injection, and typically with less than 10 ppm (parts per million) of non-volatile solutes, is routed through line 100 directly to the steam injection well.

[00103] A commercial watertube boiler 110 operating on high quality ASME rated feed water supplies the high pressure steam, through line 124, that is required to drive the high pressure high efficiency HiPVap 84 wherein the high pressure steam transfers heat by condensing on the second surface of said plurality of heat transfer surfaces. The condensing steam descends by gravity to the bottom of the tubular heat transfer surface and is collected as condensate stream 120 and then returned to the commercial watertube boiler 110 wherein energy is supplied and the condensate is returned to its steam form to keep the evaporation process going.

[00104] A small boiler blowdown stream represented by line 114 is taken from the watertube boiler 110, and directed to the HiPVap 84 for recovery. The blowdown stream 114 is necessary to prevent buildup up of total dissolved solids (TDS) in the boiler due to venting and ensuing makeup water requirement and is typically less than 2% of the boiler capacity.

[00105] Makeup water for the watertube boiler 110 can be supplied by any of various means of producing deionized water. As depicted in Fig. 4, the makeup is supplied through line 204 by a small, high recovery, typically greater than 90%, reverse osmosis (RO) unit 200 that operates on good quality service or well water. Under these circumstances, the RO unit 200 provides high quality ASME grade permeate, which along with the industry standard conventional high pressure boiler chemical program 112, ensures trouble free operation of the watertube boiler 110. In other embodiments, the RO unit 200 can be replaced with an ion exchange column, of various types, to provide the ASME quality water required by watertube boiler 110.

[00106] The just described novel HiPVap process produces a high quality steam at pressures dependent on the individual site designs, typically ranging from

200 to 1600 psig, which satisfies the 100% quality steam requirement needed for SAGD operation at a cost reduction when compared to OTSG and MVC processes. Ideally, and as depicted in Fig. 4 and 5, only one stream, HiPVap blowdown 96 needs to be handled. The blowdown, as represented by line 96, from the HiPVap, 84, can be disposed of by what is known as deep well injection, after flashing 130 to atmospheric pressure, in areas where it is permissible and/or possible, off-site waste disposal facilities, or preferentially by a zero liquid discharge (ZLD) system. The flashed steam 134 is then sent to the condenser 30 for recovery.

[00107] DESCRIPTION OF AN EMBODIMENT WITH ZLD

[00108] Referring to FIG. 5, an alternate embodiment of the present invention for the high pressure high efficiency HiPVap process on produced water is shown. It is a flow diagram for produced water that has been recovered from a steam flood process in which the amount of hardness and carbonate alkalinity are high enough that pre-conditioning is required to lower them to acceptable quantities for HiPVap operation. The zero liquid discharge (ZLD) concept is also illustrated in order to further understand the breadth of the process.

[00109] The production stream 2 coming from the well head containing a mixture of oil and water (e.g., 75% water and 25% oil), at a typical temperature of around 330° F, flows to the oil separation zone 8 after passing through the produced water pre-heater 4. After substantially all oil has been removed, typically to a residual content of 10-20 ppm by means as discussed previously, the produced water, now at a temperature around 190° F, flows via line 14 to the deionization zone 18 which incorporates weak acid cation (WAC) resins operating in the sodium form. In the WAC the calcium and magnesium cations are reduced to non-scaling levels by replacing them with sodium ions.

[00110] After calcium and magnesium removal in the deionization zone 18, the now softened produced water 24 flows to a direct contact condenser 30. In

condenser 30, the produced water mixes with and condenses the steam vapor from the crystallizing effect 162 of the multiple effect ZLD system.

[00111] After the condenser 30, the mixed stream 34 is transferred to buffer storage tank 36 where distillate 186 from the ZLD system is added.

[00112] The outlet 42 from buffer storage tank 36, now at a temperature of about 205° F is pressurized to suppress boiling and routed via line 42 through produced water pre-heater 4, which adds about 100° F to the stream, and then to degasifier 56 through conduit 50. Acid 52 is added, as appropriate and as determined necessary by the different scaling indexes, to the effluent 50 from produced water pre-heater 4 to enhance non-hydroxide alkalinity destruction. Sufficient acid is added to lower the pH where bound carbonates are converted to a free gas carbon dioxide. Then, the carbon dioxide that has been created by acid addition is removed, along with other non-condensable gasses (NCG) 58 such as oxygen and nitrogen, preferably in a flash type degasifier 56 although a forced draft type degasifier could also be utilized.

[00113] Preferably, either hydrochloric (HCl) or sulfuric (H₂ SO₄) acid is used for lowering the pH although other acids will also work. In other embodiments, wherein the different scaling indexes indicate that alkalinity removal is not required for scale free operation at elevated pH, the acid addition 52 and degasifier 56 are not utilized.

[00114] One precaution that should be observed is that both hardness and non-hydroxide forms of alkalinity should be at non-scaling levels in the produced water prior to upward pH adjustment for selected HiPVap operating conditions. Once these conditions are met, then the desired pH increase may be accomplished with any convenient caustic source, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH). Once this pretreatment has been thoroughly accomplished, then a HiPVap system can be safely operated at very high pH levels, in order to take advantage of the aforementioned silica solubility and corrosion resistance.

[00115] The treated and conditioned produced water is pressurized to the selected operating pressure with high pressure pump 70, typically 1000 psig, or greater, and directed to the high pressure high efficiency steam generator (HiPVap) 84 through blowdown heat exchanger 76. A caustic 62 (base) is added, preferably by pumped injection of liquid solution, to increase the pH of the produced feed water 66 to a pre-selected level. The pH of the produced water is raised to a selected pH of at least about 10.0, or preferably to a range between 10 and 11, or otherwise in excess of 11, and most preferably to 12 or more and is maintained, at the selected operating level, in the HiPVap process.

[00116] The HiPVap 84 and water tube boiler 110 operations have been described in detail above and will not be repeated again since there are no changes in the process itself, even with the other embodiments incorporated described here.

[00117] Makeup water for the watertube boiler 110 is supplied through line 204 by a small, high recovery, typically greater than 90%, reverse osmosis (RO) unit 200 that operates on high quality distillate from the multiple-effect ZLD system. Under these circumstances, the RO unit 200 provides high quality ASME grade permeate, which along with the industry standard conventional high pressure boiler chemical program 112, ensures trouble free operation of the water tube boiler 110. The reject stream from the RO unit 200 is routed via line 208 to the crystallizer effect 162 of the ZLD system.

[00118] The high pressure high efficiency HiPVap blowdown represented by line 96 is directed through blowdown heat exchanger 76 where it gives up heat to the incoming produced water feed in line 74. The cooled blowdown in line 104, at a typical temperature of 500° F and at ninety per cent (90%) or less of the incoming produced water flow, containing the concentrated solutes originally present in the produced water 14 along with any chemicals used to lower and raise the pH can be disposed of by the standard approach used at individual sites. This includes flashing to recover lower temperature steam for other purposes and then holding the

liquid portion on-site in waste evaporation ponds, trucking to a waste site, or injection into deep wells.

[00119] In the preferred embodiment as described herein, the blowdown stream depicted as line **104** is directed to the multiple-effect ZLD system as shown in FIG. 5 wherein increased recovery is accomplished. The first step in the ZLD process involves flashing the blowdown **104** to a lower pressure in flash tank **130**. The flash tank **130** separates the HiPVap liquid blowdown **104** into a lower temperature steam line **134** and liquid stream **138** which are routed to Effect (1) **142** which constitutes a primary concentrator evaporator. Effect (1) **142** is the first effect of effects (1), effect (2), etc, through effect (N) (wherein N is a positive integer equal to the number of effects) to successively recover a series of lower pressure steam flows which are utilized to drive evaporation in the succeeding effect. The first effects of the ZLD process gradually concentrate the blowdown from evaporator **84** prior to solute crystallization in effect (N) **162**. The concentration effects 1, 2, etc. may be falling film or rising film type evaporators while the N effect, or crystallizer, is typically of the forced circulation type.

[00120] The solutes in the recirculated blowdown stream, as represented by line **138**, are concentrated by removing water from the recirculating solution as it passes over the heat transfer surface in effect **142**. As depicted in FIG. 5, the evaporator utilizes falling thin film evaporation wherein the recirculated stream depicted by line **138** is thinly spread across the inner surface of a plurality of heat transfer tubes. A small portion of water is removed from the thin recirculating stream in the form of steam vapor driven by the flashed steam in line **134** which is transferring heat by condensing on the outside of the heat transfer tubes. The condensing steam descends by gravity to the bottom of the tubular heat transfer surface and is collected as condensate stream **160**.

[00121] The condensate stream 160 is routed through effect (2) 152 where it is combined with the distillate 170 from effect (2) 152 and then through effect (N) 162. The combined distillate/condensate 166 from all effects is then routed to the distillate heat exchanger 182 and then to storage 36 via line 186.

[00122] The steam vapor produced in effect (1) 142 is collected and directed to effect (2) 152 via line 144 to provide the driving force for evaporation. Line 148 represents the concentrated blowdown from effect (1) 142 which is recirculated across the heat transfer surface in effect (2) 152 as was described for the preceding effect. The steam vapor 154 generated is routed to effect (N) 162 where it condenses and heats the recirculating solution in a forced circulation heat exchanger. The blowdown from effect (2) 158 is recirculated through the heat exchanger in effect (N) 162 and then flashed into a chamber where the highly concentrated solutes precipitate out of solution.

[00123] Line 178 represents the concentrated blowdown from effect (N) 162 containing precipitated solids that can then be disposed of either by sending it to an on-site waste holding area for disposal or preferably in a solids dewatering device. Typical dewatering equipment consists of various type filter presses or centrifuges in which the suspended solids are removed from the mixed solution by filtration or centrifugal forces. The dewatered solids can then be trucked off either for disposal in a landfill site or, in some cases, sold for their value as inorganic salts. The filtrate is then sent back to the crystallizing effect (N) for further processing. In other installations, as applicable, the blowdown 178 is sent to a spray dryer and any water is removed from the mixed solution by the application of heat resulting in nothing left but salts of various types.

[00124] The vapor produced in the crystallizer effect (N) 162 is routed via conduit 174 to condenser 30 wherein it makes direct contact with the incoming de-oiled produced water 14 prior to storage buffer tank 36.

[00125] The final step in our novel process includes taking a portion of low solute condensate and distillate stream 186 for use as RO feed 196 after passing through heat exchanger 192. The high quality RO feed 196, which does not have any volatile organics, allows the RO unit 200 to produce ASME quality permeate water for feed to the watertube boiler 110.

[00126] It should be noted that the use of a tubular falling film evaporator design for equipment 84, 142, and 152 is provided only for purposes of enabling one skilled into this art to understand the evaporation process and is not intended to limit the process to the use of the same. Those familiar with the art will recognize that other designs, such as, for example, a rising film evaporator, or a natural, mechanical, or forced circulation evaporator, may be alternately utilized with the accompanying benefits and/or drawbacks that may be inherent in the alternative designs.

[00127] In other embodiments, and as suited to meet the particularized needs of a selected produced water chemistry, various forms of hardness removal may be utilized as long as the requirements for a resulting scale free environment in the HiPVap are met. These include a sodium form strong acid cation (SAC) exchange or a partial hardness removal utilizing a SAC exchange process followed by a polishing sodium form WAC or SAC. The benefit gained by SAC exchange is the use of sodium chloride (NaCl) as a regenerant as compared to the two-step sodium form WAC process which requires the use of acid and caustic to effect regeneration to the desired sodium form. Drawbacks of the SAC process are lower efficiencies wherein excess sodium chloride is required for regeneration resulting in a 10% to 15% increase over a WAC process, waste stream quantity for disposal, and hardness removal limitations in applications with TDS in excess of about 3000 ppm. However, there are applications where ease of use and relatively cheap cost of sodium chloride makes the SAC process a better choice than a WAC process as long as the effluent meets the scale free environment requirements for the HiPVap process.

[00128] In yet another embodiment, produced water 14 is first treated in a weak acid cation (WAC) ion exchange unit, operated in the hydrogen form where hardness and bicarbonate alkalinity are simultaneously removed. For those cases where produced water 14 hardness is greater than alkalinity, operation of the weak acid cation ion exchange unit must be facilitated by addition of a source of alkalinity, such as by addition of an aqueous solution of sodium carbonate (Na_2CO_3).

[00129] Regeneration of the resin is accomplished by use of conveniently available and cost effective acid. It is well known by those in the art that regeneration of WAC ion-exchange resins may proceed quite efficiently, at near stoichiometric levels (generally, not more than about one hundred and twenty percent (120%) of ideal levels). Preferably, hydrochloric acid may be used, since in such cases highly soluble calcium chloride would be produced, and the regeneration process would not pose the potential danger of formation of insoluble sulfate precipitates, such as calcium sulfate, even with high strength acids. However, by use of a staged regeneration procedure, i.e., by using a low concentration acid followed by a higher concentration acid, it is possible to reliably utilize other acids, including sulfuric acid (H_2SO_4), while still avoiding undesirable precipitates on the resin. In this manner, hardness ions are solubilized to form soluble salts, which are then eluted from the resin bed.

[00130] ECONOMICS OF HiPVap STEAM GENERATION

[00131] An economic analysis of the prior art systems in comparison to a preferred embodiment (FIG. 5) of the novel process disclosed herein was undertaken to further demonstrate the reduced costs that can be realized in the generation of high pressure steam. The study included the four systems as detailed in Figures 1, 2, 3, and 5 along with the following process assumptions for all cases.

[00132]	Inlet Water Analysis, as mg/l CaCO ₃ , except pH and where noted:			
[00133]	Calcium (Ca)	13	Bicarbonate (HCO ₃) ⁻	188
[00134]	Magnesium (Mg)	5	Carbonate (CO ₃)	0.3
[00135]	Sodium (Na)	1579	Sulfate (SO ₄)	0.3
[00136]	Potassium (K)	0.51	Chloride (Cl)	1410
[00137]	Silica (SiO ₂)	180	Iron (Total as mg/l ion)	1.1
[00138]	TDS	2179 as mg/l ion		
[00139]	pH	7.3	Temperature	80° C
[00140]	Oil	10-20 mg/l	Flow Rate	3750 GPM

[00141] Assumptions:

[00142] Produced water from the recovery well is available at 164° C for use within the different processes for heat exchange purposes.

[00143] All systems are zero liquid discharge (ZLD).

[00144] A once through steam generator (OTSG) has a water to steam conversion ratio of 80%.

[00145] Watertube boilers operate with a 2% blowdown rate.

[00146] Operating Cost Assumptions:

[00147] The cost of lime and magnesium oxide is the same.

[00148] The OTSGs and water tube boilers operate at the same efficiency for conversion of fuel absorbed heat. The fuel consumption, per unit heat transferred to the water, of the OTSGs and water tube boilers is the same in all cases.

[00149] Capital Cost Assumptions:

[00150] Scope of supply for all cases includes all equipment, instruments, valves, piping, and structural steel shown within boundaries of block flow diagrams.

[00151] Equipment and costs not included in the cost estimate:

[00152] Water storage tanks

[00153] Control systems (PLC, DCS, etc.)

- [00154] Motor control centers (MCC) transformers, switchgear, etc.
- [00155] Installation cost
- [00156] Infrastructure cost for foundations, underground piping, power systems, etc.
- [00157] Plant life is 30 years.

TABLE 1
UTILITIES

	FIG 1	FIG 2	FIG 3	FIG 5
Power (kw-hr/hour)	3,871	18,665	19,289	3,528

TABLE 2
CHEMICAL CONSUMPTION
(Pounds/day as 100% chemical)

	FIG 1	FIG 2	FIG 3	FIG 5
Hydrochloric Acid (HCl)	6,500	6,200	6,200	8,000
Sodium Hydroxide (NaOH)	7,000	10,200	12,200	12,100
Lime (Ca(OH) ₂)	7695	-	-	-
Magnesium Oxide (MgO)	12,000	-	-	-
Coagulant	50	-	-	-
RO Antiscalant	-	-	200	-

TABLE 3
CAPITAL COST RATIOS

	FIG 1	FIG 2	FIG 3	FIG 5
Capital Cost	1.20	1.25	1.30	1.0

TABLE 4
SLUDGE AND SALT CAKE

	FIG 1	FIG 2	FIG 3	FIG 5
Tons/Day	115	63.6	64.7	65.7

TABLE 5
UNIT PROCESS STEPS REQUIRED FOR STEAM GENERATION

	FIG 1	FIG 2	FIG 3	FIG 5
Warm Lime Softening	X			
Media Filtration	X			
Ion Exchange System	X			X
Mechanical Vapor Compression		X	X	
Primary Reverse Osmosis System			X	
Produced Water Chillers			X	
Produced Water Evaporation		X	X	X
High Pressure Produced Water Pump	X	X	X	X
Once Through Steam Generator	X	X		
Steam Separators for 100% Quality Steam	X	X		
Watertube Boiler			X	X

[00158] As can be seen in Tables 1 and 3, the power consumption and capital cost are lower when the high pressure, high efficiency HiPVap method of steam generation, as presented herein, is incorporated into the steam flooding oil recovery methods in current use. When the lower costs are included with other benefits of the HiPVap process, such as reduced complexity of operation, fewer unit processes as shown in Table 6, and increased corrosion resistance, it becomes apparent that the method, as taught herein, is a cost effective, novel, and new approach to overcoming aforementioned present day state of the art limitations and problems.

[00159] BENEFITS OF HiPVap PROCESS DESIGN AND OPERATION

[00160] Many exemplary and desirable process benefits provided by the HiPVap process design and operation were listed above. Detailed explanations of such benefits include:

[00161] (A) Fewer unit processes

[00162] It can be seen from Table 5 above that the HiPVap process is comprised of fewer individual unit operations than other steam generation processes. In the preferred embodiment as depicted by FIG. 5, the HiPVap process

consists only of the high pressure evaporator and its accompanying commercial watertube boiler as a source of heat to drive the evaporation process. This feature reduces the complexity of produced water recovery for steam generation and leads to fewer operational and maintenance hours required.

[00163] The elimination of a requirement for a once through steam generator (OTSG) carries with it additional benefits chiefly of which is its designed low water to steam efficiency. This design factor is based on the poor wetting of heat exchange surfaces exhibited in current equipment which, in turn, leads to tube burn out at high temperatures and recovery due to dry spots, and tube plugging. The HiPVap, in contrast, is designed for high salinity high scaling probability waters which, by necessity, requires that heat exchange surfaces be thoroughly wetted at all times. Therefore, the rate of recirculation water over the heat transfer surface is much greater than the rate of steam vapor generation ensuring that dry spots cannot occur and that scaling potential is minimized.

[00164] (B) Reduced Capital Cost

[00165] The lowered corrosion potential that results from operating the HiPVap process with a high pH in the concentrated circulating solution allows the use of lower cost materials for heat transfer tubes or plates and other wetted surfaces that are contacted by the concentrated solution, such as sump walls. This is an important advantage since the costs of these materials have a substantial impact on the capital cost of an evaporator. In most cases the use of high cost duplex and AL6XN (6 per cent minimum molybdenum) type stainless steels, which are normally used in high chloride salt solutions, can be eliminated in favor of lower grade materials such as carbon steel. In addition, fewer individual unit processes result in eliminated equipment and installation infrastructure costs.

[00166] (C) Reduced Operating Cost

[00167] The HiPVap process has a significant advantage over other evaporative processes in that high energy consuming mechanical vapor compressors are not required either in the steam generation phase or in the zero

liquid discharge zone. The novel design disclosed herein operates entirely on heat and the recovery of waste heat in liquid blowdown streams. Other systems require large amounts of electrical power input for operation.

[00168] Produced water plant operating costs are also reduced due to minimizing, or eliminating, costly proprietary antiscalants and/or dispersants. Additional savings can be found by eliminating the need for seeded slurry operation at installations where the calcium and sulfate ions are at a high level in the produced water feed stream. Along with the cost of seeding evaporators with calcium sulfate crystals, there is also incurred costs associated with calcium chloride and/or sodium sulfate injected chemicals to provide enough precipitating ions to maintain the seed bed at many installations. Further savings can be realized by the reduction in frequency of cleaning operations, less expensive cleaning chemicals, less downtime for cleaning, and no requirement for costly physical cleaning operations. Still further, if the ZLD option is incorporated, the cost of disposing the waste blowdown is eliminated along with the requirement for freshwater makeup necessary to maintain process flows.

[00169] It will thus be seen that the objects set forth above, including those made apparent from the preceding description, are efficiently attained, and, since certain changes may be made in carrying out the above method and in construction of a suitable apparatus in which to practice the method and in which to produce the desired product as set forth herein, it is to be understood that the invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. For example, while exemplary designs for a falling film high pressure evaporator along with hardness and alkalinity control methods have been illustrated and described, other embodiments are also feasible to attain the result of the principles of the method disclosed herein. Therefore, it will be understood that the foregoing description of representative embodiments of the invention have been presented only for purposes of illustration and for providing an understanding of the invention, and it is not intended to be exhaustive or restrictive,

or to limit the invention to the precise forms disclosed. On the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as expressed in the appended claims. As such, the claims are intended to cover the methods and structures described therein, and not only the equivalents or structural equivalents thereof, but also equivalent structures or methods. Thus, the scope of the invention, as indicated by the appended claims, is intended to include variations from the embodiments provided which are nevertheless described by the broad meaning and range properly afforded to the language of the claims, or to the equivalents thereof.

CLAIMS

1. A process for generating steam for downhole injection in a steam flood process for oil recovery, said process comprising:

(a) heating a de-oiled produced water stream containing water, dissolved solutes, and dissolved gases, said dissolved solutes further comprising at least one molecular species which is at low ionization levels when in solution at around neutral pH,

(b) raising the pH of said heated, produced water stream to maintain the solubility of said molecular species therein at a selected concentration factor,

(c) pressurizing and directing said produced water stream to a circulating concentrated brine in a produced water evaporator, said evaporator having a plurality of heat transfer surfaces,

(d) distributing said circulating brine across a first surface of at least one of said plurality of heat transfer surfaces to generate a steam vapor suitable for injection into a selected geological formation to fluidize oil,

(e) discharging at least some of said brine as an evaporator blowdown stream,

(f) distributing steam from a watertube boiler across a second surface of at least one of said plurality of heat transfer surfaces to condense said steam as a condensate,

(g) returning said condensate to said watertube boiler for steam production, and,

(h) discharging at least some of said condensate as a boiler blowdown to the produced water evaporator.

2. The process as set forth in claim 1, wherein said dissolved solutes further comprise hardness cations in a quantity that produces a scale deposition on said first surface of said heat transfer surfaces at said selected concentration factor.

3. The process as set forth in claim 1, wherein said produced water stream further comprises at least some non-hydroxide alkalinity.
4. The process as set forth in claim 1, wherein the pH is raised to between 10 and 11 and maintained in said evaporator circulating brine.
5. The process as set forth in claim 1, wherein the pH is raised to between 11 and 12 and maintained in said evaporator circulating brine.
6. The process as set forth in claim 1, wherein the pH is raised to between 12 and 13 and maintained in said evaporator circulating brine.
7. The process as set forth in claim 1, wherein the pH is raised to greater than or at least about 13 and maintained in said evaporator circulating brine.
8. The process according to claim 1, wherein the step of raising the pH is accomplished by addition of an inorganic base in aqueous solution, said base selected from the group consisting of sodium hydroxide, and potassium hydroxide.
9. The process as set forth in claim 3, wherein a portion or substantially all non-hydroxide alkalinity in said produced water stream is removed.
10. The process as set forth in claim 9, wherein the step of removing said non-hydroxide alkalinity, is further comprised of lowering the pH of said produced water stream to release at least some free carbon dioxide.
11. The process as set forth in claim 10, wherein the step of adjusting pH is accomplished by the addition of hydrochloric acid or sulfuric acid.
12. The process according to claim 1, wherein said produced water evaporator comprises a falling thin film evaporator, operating as a single unit, or operating in parallel, to generate said steam and said blowdown stream.
13. The process according to claim 1, wherein said produced water evaporator comprises a rising film or thermo-siphon evaporator, operating as a single unit, or operating in parallel, to generate said steam and said blowdown stream.
14. The method according to claim 1, wherein said heat transfer surfaces are tubular.

15. The method as set forth in claim 14, wherein said heat transfer surfaces are operated in a vertical position.

16. The method as set forth in claim 14, wherein said heat transfer surfaces are operated in a horizontal position.

17. The method as set forth in claim 14, wherein said heat transfer surfaces are designed for enhanced heat transfer.

18. The process according to claim 1, wherein said produced water evaporator comprises falling film and rising film in a combined process, operating as a single unit, or operating in parallel, to generate said steam and said blowdown stream.

19. The process as set forth in claim 14 wherein said circulating brine is heated on the interior of the tubes.

20. The process as set forth in claim 14 wherein said circulating brine is heated on the exterior of the tubes.

21. The process as set forth in claim 1, further comprising distributing said circulating brine across a first heat transfer surface of at least one of said plurality of heat transfer tubes to generate a steam vapor.

22. The process as set forth in claim 21, further comprising collecting said steam vapor and directing it to an injection well present in a selected geological formation, to produce an oil and water mixture.

23. The process as set forth in claim 21, wherein said steam vapor generated is at a pressure ranging from 200 to 1600 psig.

24. The process as set forth in claim 1, further comprising the step of treating said produced water evaporator blowdown stream in a zero liquid discharge process.

25. The process as set forth in claim 1, further comprising the step of injecting said produced water evaporator blowdown stream in a deep well for disposal.

26. The process as set forth in claim 24, wherein said zero liquid discharge comprises a steam driven multiple effect concentration and crystallization evaporator process to generate (a) high quality steam vapor and, (b) a high solute, high suspended solids slurry.

27. The process as set forth in claim 1, further comprising supplying said water tube boiler with de-ionized makeup water to produce said steam and a high solute containing blowdown stream.

28. The process as set forth in claim 27, wherein said de-ionized makeup water is produced by a reverse osmosis unit.

29. The process as set forth in claim 26, further comprising, dewatering said generated suspended solids slurry in a filter press or belt filter and, further comprising, recycling the filtrate back to the crystallization effect of the multiple effect evaporator.

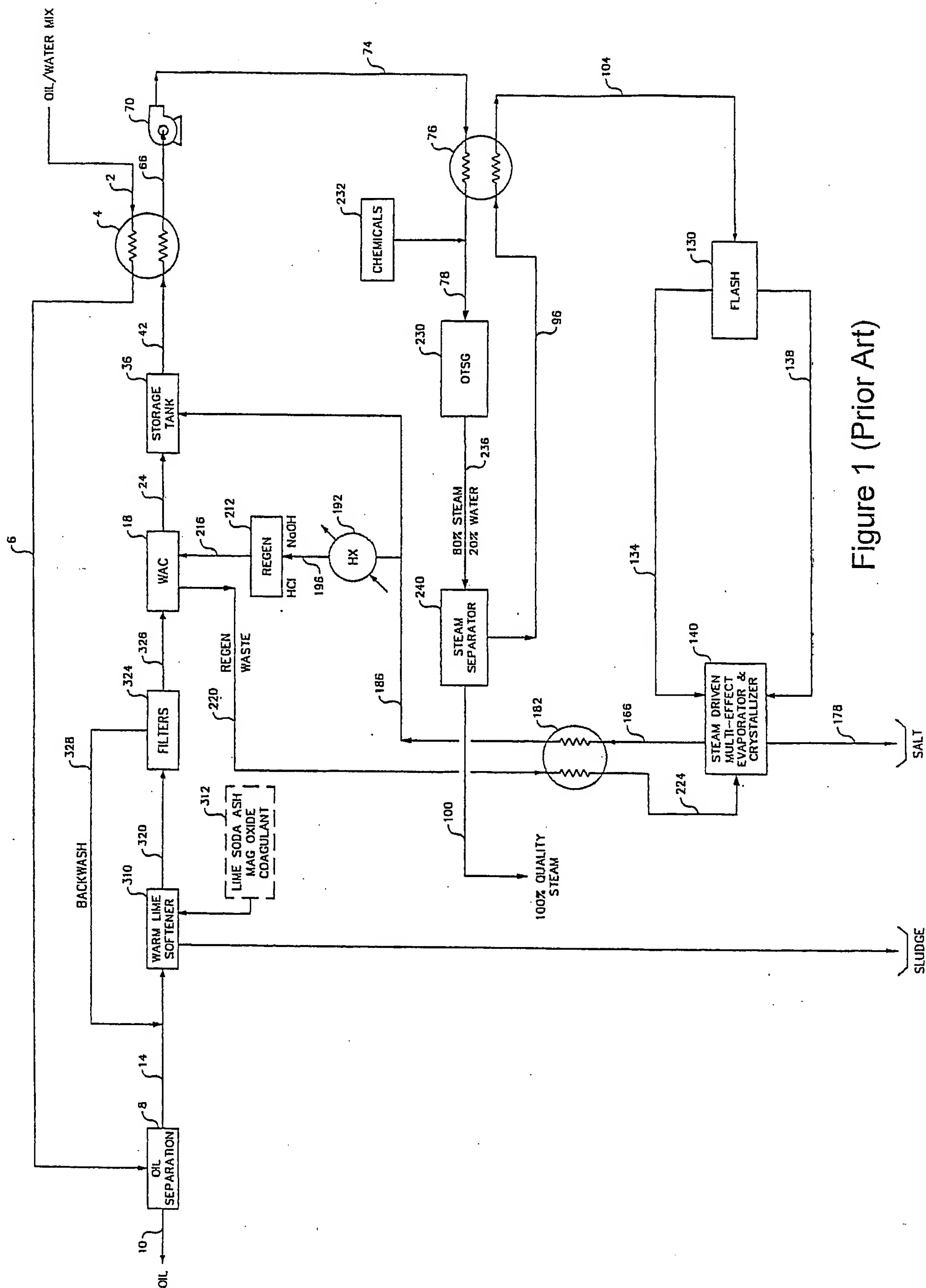
30. The process as set forth in claim 24, wherein said zero liquid discharge comprises a steam driven crystallizer evaporator process to generate (a) high quality steam vapor and, (b) a high solute, high suspended solids slurry, and, further comprising, dewatering said generated suspended solids slurry in a filter press or belt filter and, further comprising, recycling the filtrate back to the inlet of the crystallizer evaporator.

31. The process as set forth in claim 27, wherein said de-ionized makeup water is produced by an ion exchange unit.

32. The process as set forth in claim 28 or claim 31, wherein the feed water utilized for de-ionized makeup water is fresh water.

33. The process as set forth in claim 2, wherein a portion or substantially all hardness cations are removed in a deionization zone.

34. The process as set forth in claim 1, wherein said molecular species is silica.



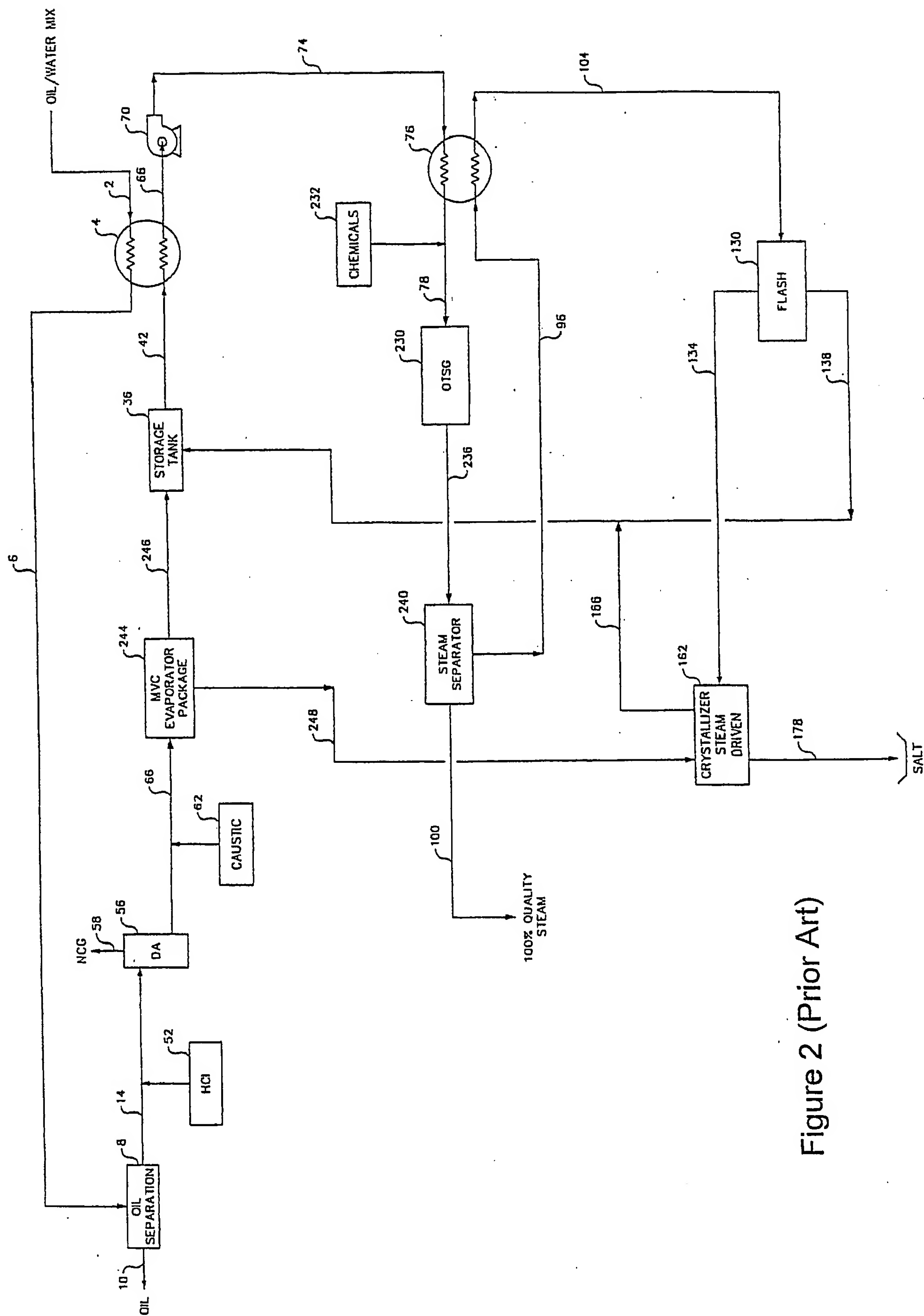
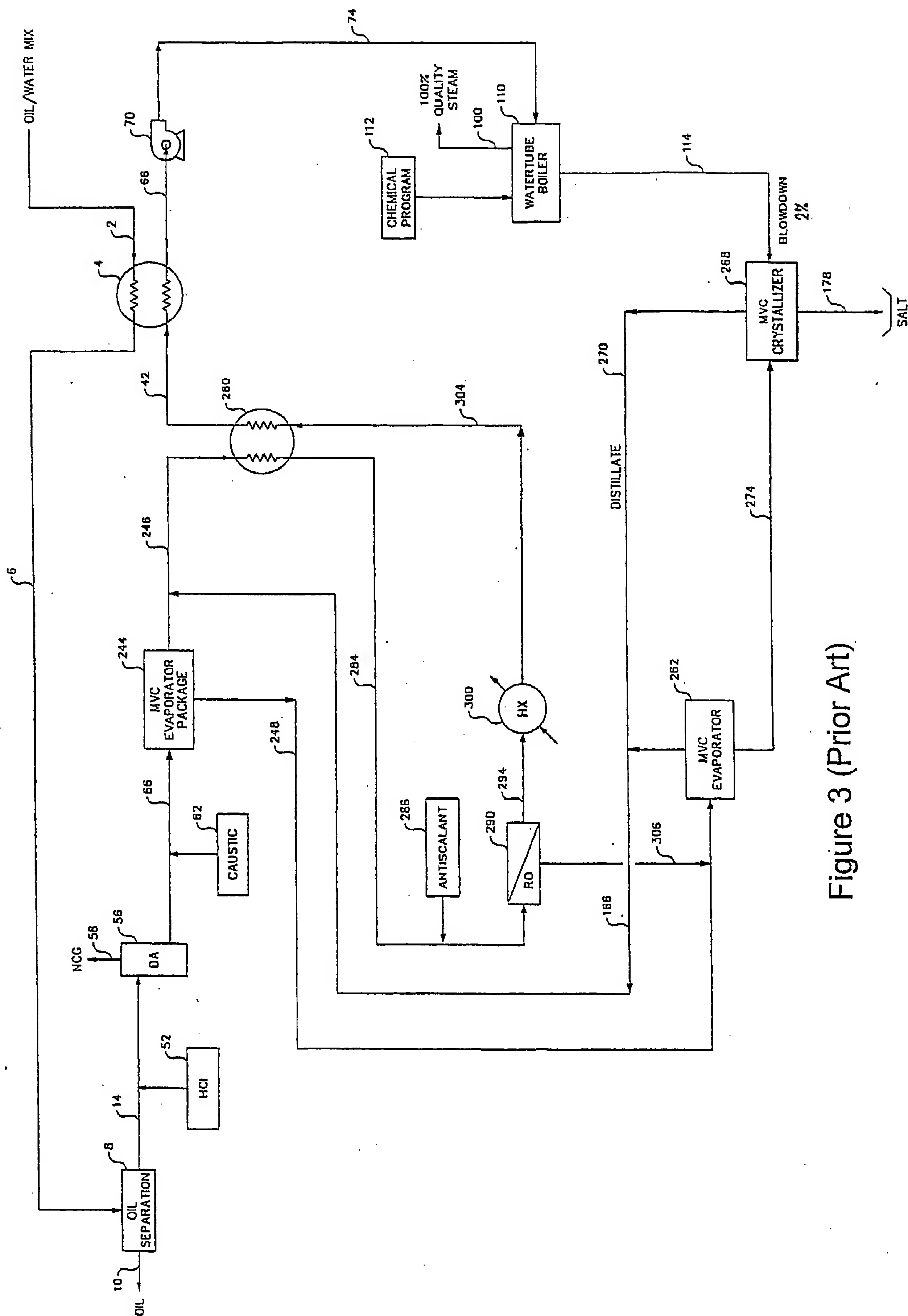


Figure 2 (Prior Art)



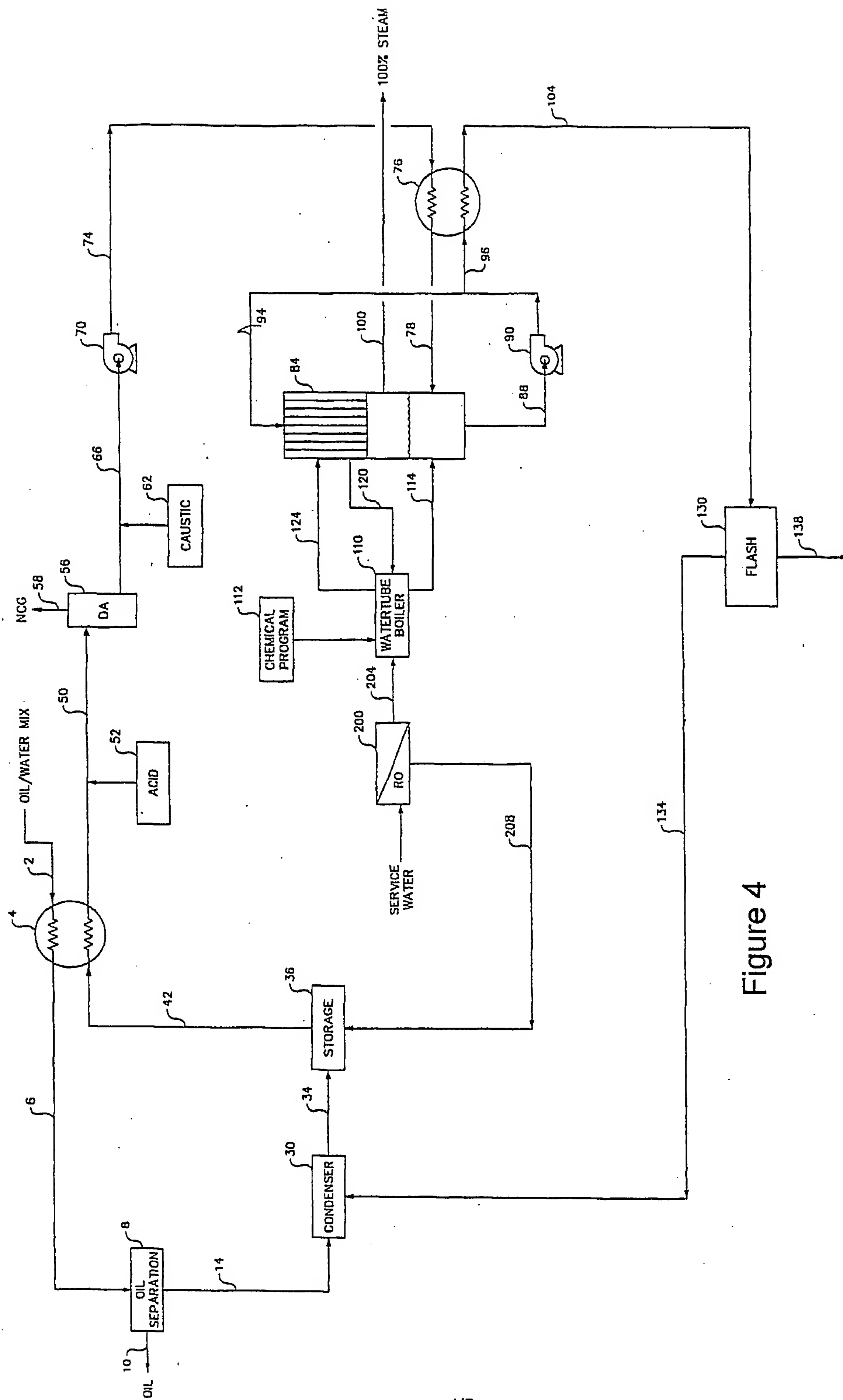


Figure 4

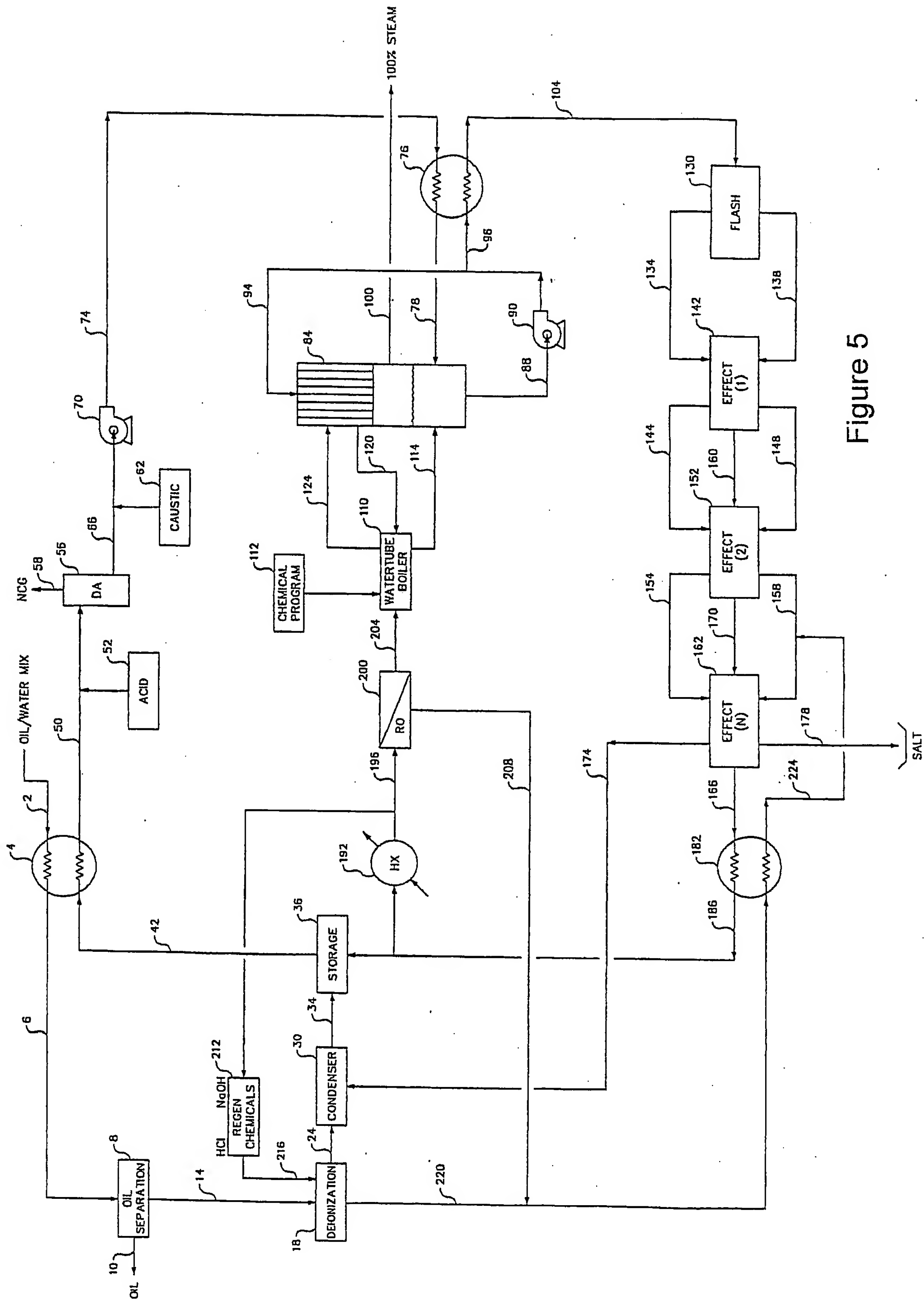


Figure 5

Figure 6

**TYPICAL ONCE THROUGH STEAM GENERATOR
FEEDWATER REQUIREMENTS**

Chlorides	<1000 mg/l
Hardness (as CaCO ₃)	<0.5 mg/l normal <1.0 mg/l maximum
Oil and Grease	<0.5 mg/l normal <1.0 mg/l maximum
TDS	<2500 mg/l
Silica (as SiO ₂)	<80 mg/l
TSS	<1.0 mg/l
Iron (as Fe)	<0.1 mg/l
pH	9.0 – 10.0
H ₂ S	<0.1 mg/l
Oxygen	Zero

Figure 7

**TYPICAL 1000 PSIG WATERTUBE BOILER
ASME FEED and BOILER WATER REQUIREMENTS**

Feedwater	
Hardness (as CaCO ₃)	<0.05 mg/l
Non-Volatile TOC (as C)	<0.20 mg/l
Oil and Grease	<0.20 mg/l
Copper (as Cu)	<0.01 mg/l
pH	8.8 – 9.6
Boiler Water	
Silica (as SiO ₂)	<6 mg/l

Ionization of Silica

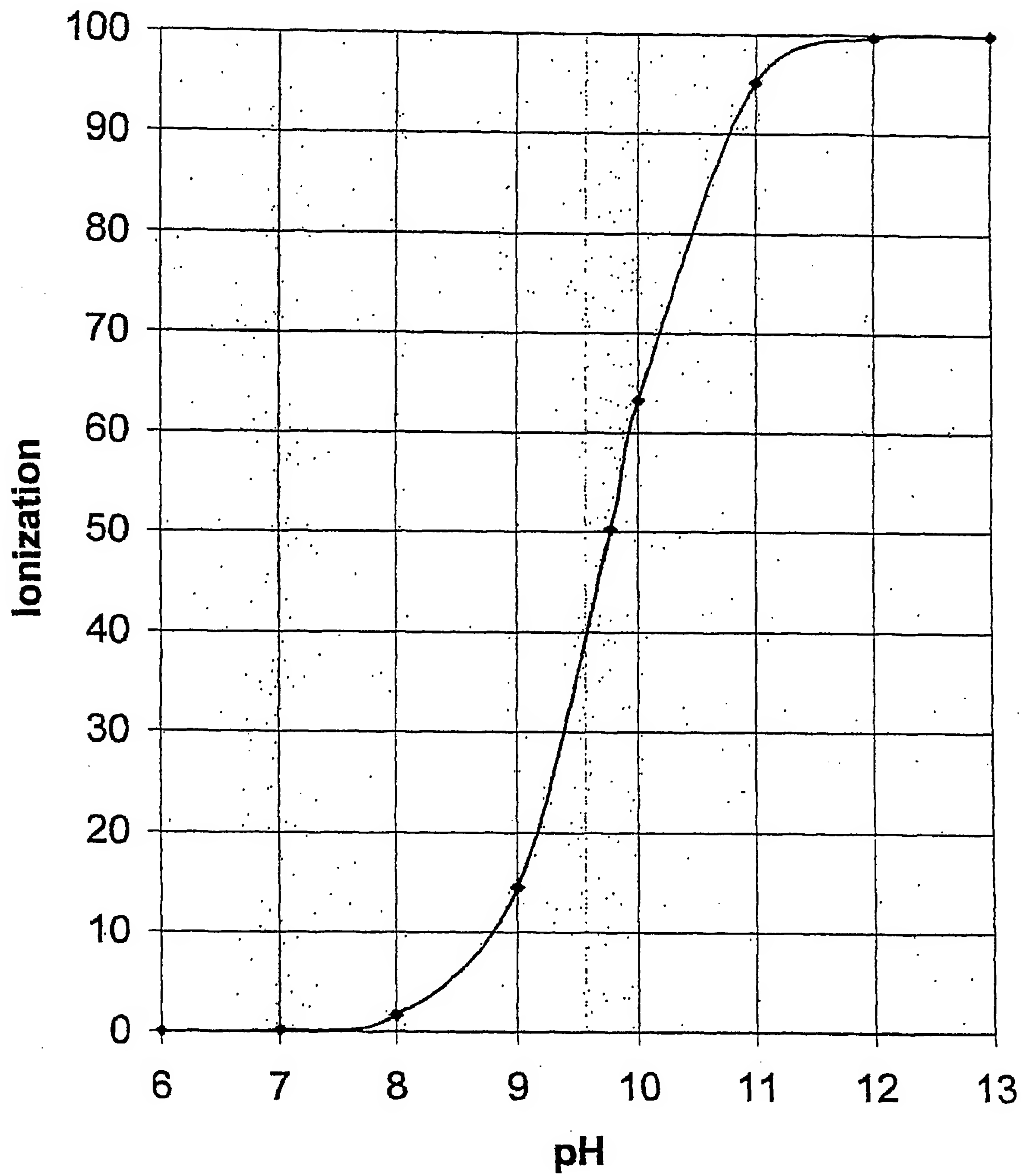


Figure 8

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Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

PTO/SB/01

**DECLARATION
FOR UTILITY OR DESIGN
PATENT APPLICATION**

Attorney Docket Number **4553-00025**
First Named Inventor **Keith R. Minnich et al**

COMPLETE IF KNOWN

Application Number **10/580,812**
Filing Date
Group Art Unit
Examiner Name

Declaration
☐ Submitted with
Initial Filing

Declaration
☒ Submitted after
Initial Filing

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Method for Production of High Pressure Steam from Produced Water

(Title of the Invention)

the specification of which

☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY)

11/24/2004

as United States Application Number or PCT

International Number
(if applicable).

PCT/US2004/039515

and was amended on (MM/DD/YYYY)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under Title 35, United States Code §119(a)-(d) or §365(b) of any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or §365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent, inventor's or breeder's rights certificate(s), or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Copy Attached?	
				YES	NO
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

☐ Additional foreign application numbers are listed on a supplemental priority sheet attached hereto:

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)	Additional provisional <input type="checkbox"/> Application numbers are listed on a supplemental priority sheet attached hereto.
60/525,578	11/26/2003	

Type a plus sign (+) inside this box [+]

Attorney Docket Number 4553-00025

DECLARATION

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §365© of any PCT international application designated the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States of PCT International application in the manner provided by the first paragraph of Title 35, United States Code §112. I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)

☐ Additional U.S. or PCT international application numbers are listed on a supplemental priority sheet attached hereto.

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

☒ Customer Number: 26753

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Thomas M. Wozny	28,922	Christopher M. Scherer	50,655
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor: ☐ A petition has been filed for this unsigned inventor

Given Name (first and middle (if any))

Keith R.

Family Name or Surname

Minnich

Inventor's Signature

Date

Residence: City

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☒ Additional inventors are being named on supplemental sheet(s) attached hereto.

Please type a plus sign (+) inside this box [+]

Attorney Docket Number	4553-00025
------------------------	------------

DECLARATION	ADDITIONAL INVENTOR(S) Supplemental Sheet
--------------------	---

Name of Additional Joint Inventor, if any:		<input type="checkbox"/> A petition has been filed for this unsigned inventor	
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City Lake Mary	State FL	Zip 32746	Country US

Name of Additional Joint Inventor, if any:		<input type="checkbox"/> A petition has been filed for this unsigned inventor	
Given Name (first and middle [if any]) Richard M.		Family Name or Surname Schoen	
Inventor's Signature		Date	
Residence: City Hartland	State WI	Country US	Citizenship United States
Mailing Address N67 W29767 Hartling Road			
City Hartland	State WI	Zip 53029	Country US

<input type="checkbox"/> Additional inventors are being named on supplemental sheet(s) attached hereto.

August 21, 2000

Keith Minnich
W291 N3821 Roundhill Road
Pewaukee, WI 53072

Dear Keith:

Aquatech International Corporation is pleased to present to you the following offer of employment and employment agreement, conditioned upon the closing of the Acquisition on or before August 31, 2000. Following are the terms and conditions of your anticipated employment at the close of the Acquisition.

This Employment Agreement (the "Agreement") is by and between Aquatech International Corporation, a Pennsylvania corporation (the "Company" or "Aquatech") and Keith Minnich (the "Employee"). In consideration of the mutual promises set forth, and intending to be legally bound, the Company and the Employee agree as follows:

1. **Duties**

Employee's title, duties and responsibilities shall be those defined in Schedule A of the Agreement and the Employee will devote 100% of his professional work efforts to Aquatech International Corporation (and Aqua-Chem via Aquatech International Corporation through December 31, 2001). The amount of time devoted to professional work efforts for Aquatech can be adjusted every 6 months subject to mutual agreement.

2. **Compensation**

While the Employee remains in the Company's employ, the Company agrees to pay to the Employee, and the Employee agrees to accept the compensation and benefits listed in Schedule B of the Agreement which is attached and incorporated as part of the Agreement. Compensation can be adjusted every 6 months to reflect the amount of time devoted to professional work efforts for Aquatech

3. **Term of Agreement**

The Agreement shall become effective upon the successful closing of the Acquisition and continue in full force and effect until March 1, 2003 unless time devoted to Aquatech drops below 75%, at which time the agreement would be amended to mutual agreement.

4. **Termination of Employment**

a.) The Employee's employment can be terminated by Employee's death, disability or by the Employee's voluntary separation. The Company may terminate the Employee during the term of the Agreement with or without "cause". For purposes of the Agreement the term "cause" shall mean any of the following as determined by the Company in the exercise of good faith and reasonable judgment (i) the willful and continued refusal by the Employee to perform the Employee's duties hereunder, other than by reasons of health, after a written demand for such performance is delivered to the Employee by the Company that identifies the manner in which the Employee has refused to perform the Employee's duties, (ii) the commission of an act by the Employee constituting a felony under state or federal law, (iii) the habitual abuse by the Employee of any substance (such as narcotics or alcohol) which materially affects the Employee's ability to perform the Employee's duties, or (iv) the Employee's engaging in an act of fraud, dishonesty, or gross misconduct in connection with the business of the Company, or (v) conduct by the Employee constituting a material breach of this Agreement. If the Employee terminates his employment for any reason, including death or disability, or if the Employee is terminated for "cause" by the Company, the Employee will not be entitled to receive any compensation or benefits after the effective date of such termination except for life insurance and disability insurance benefits and except as noted in Schedule B - Compensation.

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- b.) In the event of the Employee's termination of employment by the Company without "cause", the Company shall provide the Employee with severance as outlined in Schedule C of the Agreement (attached).
- c) The Employee acknowledges and agrees that Aquatech's Acquisition of certain assets of Aqua-Chem, Inc.'s water technologies division is motivated to acquire certain processes, know-how and information that is critical to the Industrial Concentration and Desalination business (including ZLD applications), of which the Employee has intricate background, knowledge and information. As a result of such background, the Company is willing to provide the Employee with this Agreement in reliance that the Employee will provide such background, knowledge and information regarding the Industrial Concentration business to the Company and its employees during the term of the Agreement. The Employee further acknowledges that if the Employee:
- commits a material breach of the Agreement,
 - terminates employment excluding Employee's death or disability, prior to the expiration of the term of the Agreement, or
 - is terminated for "cause" prior to the expiration of the term of the Agreement,

the Employee shall cause the Company to suffer serious and irreparable damage, and therefore, agrees to pay the Company within thirty (30) days of his or her separation any sign-on bonus. He will also forfeit any incentive accruals unpaid.

5. Confidentiality

- a.) The Employee acknowledges and agrees that certain techniques, manufacturing equipment, and processes have been developed by Aqua-Chem (including Industrial Concentration, ZLD applications, and Desalination business) or by Aquatech which have achieved the status of trade secrets, and that additional trade secrets may be developed during the course of his or her employment; and the Employee agrees not, without approval of the Company, to publish or otherwise disclose or authorize anyone else to publish or disclose either during the term of employment or thereafter, any information, knowledge or data of the Company or its customers, vendors or any other third party with whom the Company conducts business, which the Employee may receive or develop during the course of employment relating to inventions, discoveries, formulas, processes, machines, manufacturers, compositions, computer programs, accounting methods, information systems or business or financial plans or reports, marketing strategies, pricing information, customer lists, prospective customer lists, or other matters which the Employee becomes aware of in the course of employment under this Agreement or heretofore with any company controlled by others.

Confidential Information shall not include information that (a) was in the public knowledge at the time of disclosure; (b) was in the knowledge of the receiving party at the time of disclosure; or (c) becomes available to the receiving party on a non-confidential unrestricted basis from a source other than the disclosing party.

- b.) Non-Disclosure of Confidential Information. The Employee agrees that the Employee shall not use, disclose or make available to anyone for use outside the Company's organization at any time, either during the Employee's employment with the Company or subsequent to the termination of the Employee's employment such Confidential Information.

6. Return of Materials

The Employee will at anytime and upon termination for whatever reason immediately return to the Company all Company property without retaining copies.

8/31/00 *[Signature]*

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7. Ownership of Products and Inventions

- a.) The Employee acknowledges and agrees that he shall have no rights of any kind in any products purchased, produced, licensed or sold by the Company (the "Products"). The Employee hereby assigns to the Company any rights in the Products that may be granted the Employee by law (including, without limitation, patent, copyright and trademark laws) or by any other person or entity and agrees to execute any documents necessary to transfer any such rights to the Company.
- b.) As one of the conditions to the Employee's employment with the Company and in partial consideration of the payment by the Company to the Employee of such compensation as set out in the Agreement, the Employee agrees that any inventions or improvements capable of use in connection with the business, work, or investigations of the Company, which the Employee may take, invent, acquire or suggest during employment by the Company (whether or not at the request or upon the suggestion of the Company and whether or not during regular hours of work or otherwise during the term of the Employee's employment by the Company) shall become the absolute and exclusive property of the Company. The employee agrees forthwith to assign to the Company full and exclusive rights to any discovery or invention and to any patent to the full end of the term of such patent. The Agreement shall apply to all discoveries or inventions, related to anything used with the present business of the Company in principal or result. Furthermore, upon the request of the Company, the Employee shall execute all documents necessary or advisable in the opinion of the Company to direct the issuance of patents to the Company or to vest title in the Company to such inventions or discoveries. However, the expense of securing any such patent shall be borne by the Company. Finally, the Employee agrees to hold any secret process, formula, methods, or appliances for which no patent is issued as trustee for the benefit of the Company.

8. Restrictive Covenants

The Employee acknowledges that the Company, at considerable expenditure of time and money, has developed and will develop and provide and/or disclose to the Employee certain Confidential Information as defined in paragraph 5 above and trade secrets. This information is critical to the Company's business and business advantage in providing water and wastewater treatment systems, including Industrial Concentration systems. The Employee further acknowledges that the Company conducts business throughout the United States and internationally.

- a.) The Employee shall not disclose any Confidential Information, directly or indirectly, during the Employee's employment or at any time thereafter, except as required during the performance of the Employee's duties.
- b.) The Employee further acknowledges and expressly consents that during the Employee's employment and for twelve (12) months following the termination of the Employee's employment for whatever reason, the Employee, except as required during the performance of the Employee's duties under the provisions of the Agreement shall not, directly or indirectly, in any role or capacity, solicit, assist in the solicitation of or accept any business related to products and services which compete with the Company's products and services from any customer who, during the twelve (12) months prior to the termination of the Employee's employment, had been customers of Aqua-Chem or the Company; or disclose to any person, or business entity of any kind the names or addresses of any such customer; or, directly or indirectly, request, suggest or advise any such to withdraw or cancel any of their business or refuse to continue to do business with the Company. Notwithstanding the above, if the employee's employment is terminated by the Company without cause the applicable length of this non-solicitation provision shall be limited to the length of time that the employee receives severance payments from the Company (Schedule C)

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- c.) The Employee expressly consents that during the Employee's employment and for twelve (12) months following the termination of the Employee's employment for whatever reason, the Employee except as required during the performance of the employee's duties under the provisions of the agreement shall not engage, directly or indirectly, in any activities, whether as employer, proprietor, partner, stockholder (other than the holder of less than 1% of the stock of a corporation the securities of which are traded on a national securities exchange or in the over-the-counter market), director, officer, employee, consultant, agent, principal, or otherwise, in competition with the business of the Company throughout the United States or Internationally. Notwithstanding the above, if the employee's employment is terminated by the Company without cause the applicable length of this non-competition provision shall be limited to the length of time that the employee receives severance payments from the Company (Schedule C)
- d.) The Employee expressly consents that during the Employee's employment and for twelve (12) months following the termination of the Employee's employment for whatever reason or for the period of 12 months following the term of the agreement, the Employee, shall not, directly or indirectly, solicit, assist in the solicitation of, hire, or assist in the recruiting of any person employed as an employee or agent of the Company.
- e.) The Employee further acknowledges that in the event of the Employee's termination for any reason, the Employee will be able to earn a livelihood without violating the foregoing restrictive covenants and that the Employee's ability to earn a livelihood without violating such restrictive covenants is a material condition to Employee's acceptance of the Agreement.
- f.) The Employee acknowledges, agrees and expressly consents to submit to equitable injunctive relief if the Employee violates this Paragraph 8 or any other paragraph of the Agreement. This remedy of equitable injunctive relief is in addition to any other remedies at law or equity which the Company may have for breach of the Agreement by the Employee. The Employee acknowledges, agrees and expressly accepts responsibility for any attorney's fees incurred by the Company to enforce or obtain relief under the terms of this paragraph or any other provision of the Agreement or if the Employee loses any associated suit against the Company. The Company agrees to pay legal fees incurred by the Employee in the event there is a breach of agreement by the Company or if the Company loses any associated suit. The Employee agrees that the provisions of this Paragraph 8 are to be effective whether the Employee terminates the employment relationship for any reason or the Company terminates the Employee's employment for cause.
- g.) The Company acknowledges that the Employee may have personal business interests. The Company acknowledges that said business interests, if generally known to the Company, do not violate paragraph 8, unless such business interests are in competition with the businesses engaged in by the Company or business the Company has planned to engage in or the Schedule A - Employee's Duties and Responsibilities. Furthermore, the Employee agrees that such personal business interests do not violate the covenants of the Acquisition Agreement between Aqua-Chem and Aquatech International Corporation.

9. **No Assignment; Assumption**

The Agreement shall be binding upon and inure to the benefit of the successors and assigns of the company. In the event of a future disposition of the Company or including the properties and business of the Company by merger, consolidation, sale of assets, then the Company shall require the acquiring or surviving corporation to assume in writing all of the obligations of the Company hereunder. The Agreement shall inure to the benefit of and be enforceable by the Employee or his legal representatives, executors, heirs or administrators. The Employee may not assign any of his duties, responsibilities, obligations or positions hereunder to any other person.

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10. **Choice of Law and Forum**

The Employee and the Company agree and expressly consent that the Agreement shall be governed by and construed in accordance with the laws of the United States of America and the Commonwealth of Pennsylvania, without regard to principles of conflicts of law.

11. **Severability**

If any term or provision of the Agreement shall be held to be invalid or unenforceable for any reason, such term or provision shall be ineffective to the extent of such invalidity or unenforceability without invalidating the remaining terms or provisions of the Agreement

12. **Prior Agreements or Modification**

The Agreement supersedes any and all prior agreements, written or oral, between the Employee and the Company concerning the Employee's employment and related matters; No waiver or modification of the Agreement shall be valid unless in writing and duly executed by the parties.

13. **Entire Agreement**

The Agreement and its attached Schedules A, B and C contains the entire understanding of the parties hereto with respect to the subject matter hereof.

14. **Construction**

The Agreement will not be construed more strictly against one party than against another party merely by the fact that it may have been prepared by one of the parties, being it recognized that both parties contributed materially and substantially to its preparation.

15. **Other Obligations**

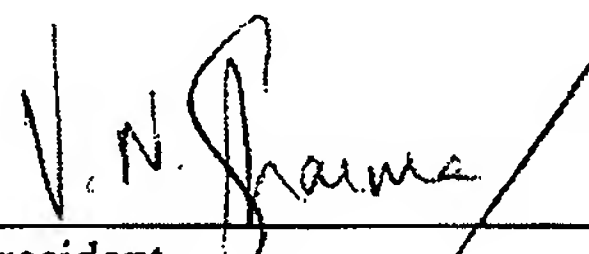
The Employee represents and warrants to the Company that he is not now under any obligation to any person, firm, corporation, or other entity, and has no interest which is known to be in conflict with his duties and obligations, the terms and conditions of which would prevent, limit, or impair in any way the performance by him of any of the covenants or duties set forth herein. However, the Company acknowledges that the Employee may render services to others, may have an interest in another business, or go into business for himself, as long as these interests do not compete with the business interests that the Company is engaged in or has planned to engage in or the Schedule A - Employee's Duties and Responsibilities.

16. **Waivers**

No waiver by either party of any breach of nonperformance of any provision or obligation of the Agreement shall be deemed to be a waiver of any preceding or succeeding breach of the same or any other provision of the Agreement.

If you are in agreement with the terms and conditions of the Agreement contained herein, please confirm your agreement to these terms and conditions by executing this Agreement on the line below, at which point the Company and the Employee will be bound by the terms hereto upon the closing of the Acquisition.

Very truly yours,

 8/31/00

President

Accepted and agreed to be legally bound,
this 31 day of Aug, 2000.



Employment Agreement between Aquatech International Corporation and Keith Minnich

Schedule A – Employee's Duties and Responsibilities

Subject to the terms, conditions and provisions of the Agreement, the Company hereby agrees upon the closing of the Acquisition, to employ Keith Minnich as Vice President, or any other comparable position or title as assigned by the Company. This position is for the Aqua-Chem IC division of Aquatech. You will report to V.N. Sharma. Any subsequent changes or modifications to the duties listed below will be made with mutual agreement between Employee and Company.

Duties and Responsibilities

The responsibilities that I would like for you to undertake as VP will be to lead and provide direction to the following key areas of the company:

- Sales and Marketing
 - Engineering (Process, Basic, Mechanical and Electrical)
 - Project Management and Procurement
 - Manufacturing
 - Commissioning
 - Quality Management
 - Product Development
-

All of these areas are key to the company's long term success and require systematic and visionary leadership. You will have P & L responsibility for the Industrial Concentration Division.

An expanded Job Description will be created prior to commencement of full operations of the division.

Areas that I would like to highlight at this time are as follow:

- It is understood that during the first phase of operations, there will be a sharing of various cross-functional resources from Aquatech Pure Water Systems Division in order to keep costs reasonable. As we establish a niche in our target markets, you will be responsible for prudent ramp up of direct resources for the IC division.
- You will be actively involved in Sales and Marketing Strategy and will be responsible for acceptance of client orders including contract review.
- You will be involved in sales promotion for the division as required.
- Establish effective standards for repeatability/modularity and input into WATERTRAK
- Implement a product culture with regard to the design of our current product
- Implement a culture which is focused on effective design review and making progress based on a product feedback loop (global lessons learned vs. just fighting fires on particular projects)
- Promote a work environment based on speed, simplicity, teamwork, and responsibility.
- Ensure proper management of project budgets and schedules. This includes ensuring that the contracts are executed on time and within budget without compromising quality.
- Interface with our client in a manner conducive to enhancing the professional image of Aquatech.
- Develop and implement internal systems that enable the accurate, cost-effective procurement of parts and equipment in sufficient time to facilitate timely fabrication and assembly.
- Ensure that cost effective purchasing contracts are developed with major suppliers.
- Coordinate the activities of commercial personnel engaged in handling the commercial activities of the division. This includes responsibility for invoicing and for the taxes and duties associated to commercial transactions.
- Make certain that the quality goals and standards of the company (ie: ISO 9001) are incorporated into the daily operation of each employee under your direction.

Handwritten signature and date: 8/31/00

Handwritten signature and date: KRM 31 Aug 00

- You will be responsible for developing an overhead budget with our corporate finance group and ensuring adherence to the same.
- Continually review resource requirements to meet divisional requirements.
- Represent the Company as directed in its relationships with customers and/or suppliers
- Provide technical direction to others as required.
- Position may require extended periods of operating a personal computer or computer design equipment as a normal part of job duties.
- Travel as necessary to participate in meetings relevant to division business.

This is a very important position to Aquatech, and demands strong personality and management skills. You will be expected to be a key factor in the cultivation of corporate culture, and the development of future growth. It is very important for you to manage effectively while supporting the Vision , mission, goals, and objectives established by Aquatech.

The Employee also shall use his best efforts to promote the interests of the Company.

The Employee shall not accept other employment or permit his personal business interests to interfere with his duties hereunder unless otherwise expressly agreed upon with Aquatech. Any personal business interests shall be generally known to the Company and shall not compete with the business interests that the Company is engaged in or has planned to engage in.

The Company desires that you relocate to the Greater Pittsburgh Metropolitan Area within the next twelve (12) months. Relocation is not mandatory; it is subject to mutual agreement. If this is mutually agreeable between both parties, then the Company will provide support and services to facilitate such relocation to Pittsburgh.

Company Signature and Date: V. N. Sanna 8/31/00

Employee Signature and Date: Kathy K. Minnick 31 Aug 00

Employment Agreement between Aquatech International Corporation and Keith Minnich

Schedule B – Compensation

Salary:

\$115,500 per year, payable in accordance with the Company's general salary payment policies. In addition, the employee will receive a sign-on bonus of \$5,500.

Incentive Plan

You will be eligible to participate in the AT/Aqua-Chem IC Incentive Plan. Your target will be 25% of your base salary. The amount of incentive bonus begins with 50% of the bonus paid when the minimum expected financial performance of the Industrial Concentration profit center has been achieved. The bonus amount will increase in a straight line progression up to 100% of bonus paid when the target performance is achieved. Additional bonus will be paid at a greater rate for financial performance beyond the target performance. The "expected financial performance" and the "target performance" will be mutually agreed and documented. Targets for bonus measurement in subsequent years will be mutually agreed upon prior to or during the comprehensive performance review of the previous year. Additional details of the plan will be mutually agreed and normalized.

In the event of termination without cause, or in the event of death or disability, any earned but unpaid incentive bonus will be paid.

The Employee will be paid any incentive bonus earned during the contract but unpaid if the Employee is on the payroll on the last day of the

Hire Date

The Employee's length of service for determining vacation and 401(K) benefits at the Company is based upon the Employee's hire date at Aqua-Chem. If the Employee separated from Aqua-Chem and was re-hired, then the credited length of service for the start of this Agreement will be the same length of service recognized by Aqua-Chem.

Job Performance Appraisals & Pay Reviews

The current practice at Aquatech International Corp. involves a comprehensive performance review every 12 months with an interim review six months in between. Pay reviews are scheduled in January or July depending upon your start date at AIC.

In your case, you will receive an interim review in March-April, 2001 and a comprehensive review in September-October, 2001 with pay review effective January, 2001 and 2002. This is subject to revision based on Company Policy. Aquatech guarantees that base salary of the employee will increase a minimum of 2.5% annually.

Vacation:

The Company agrees to provide the Employee with 20 days paid vacation per year, to be accrued in accordance with the Company's vacation policy. Three additional vacation days will be available during the calendar year as an adjustment for the difference in paid holidays between Aqua-Chem and Aquatech. Full vacation allotment for year will be made available January 1. Use of vacation days will debit vacation balance and balance will be reflected on payroll stubs. At time of termination of employment, Aquatech will pay on a pro-rated basis any unused vacation days. Prior length of service at Aqua-Chem will be recognized in determining continued vacation accrual after the term of this agreement with no reduction in current allocation.

Vacation days for 2000 will be pro-rated from the effective date of this Agreement until the end of 2000. All three of the additional vacation days provided as an adjustment between paid holidays of Aqua-Chem and Aquatech will be further added onto the pro-rated vacation for 2000.

V. N. Sharma
8/31/00

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31 Aug 00

Benefits:

Benefits for the Employee and his or her dependents, less applicable monthly cost sharing, including, but not limited to, health care insurance, life insurance, retirement plans, and other similar or comparable benefits as may be maintained by the Company from time to time, and made available to the Company's employees. The Company reserves the right to alter, amend or terminate any and all benefit plans and provide Employee with any substitute plans that it may make available to the Company's employees from time to time.

Health Benefits:

The following employer paid benefits will be provided to you and your family:

- Medical Insurance (Blue Card 250) provided at current monthly premium rates in effect for the employees of Aqua-Chem., Inc. Any increases in health insurance cost for the year 2001 and 2002 will be distributed between employer and employee on the same pro-rata basis as the current Blue Card 250 plan.
- Dental Insurance (Comparable)
- Sick Leave - Employee will receive paid sick days for any non-consecutive days of absence due to illness when proper notification (within two hours of start of scheduled work day) is provided to the Employee's supervisor. Consecutive days of illness are subject to provisions under short-term disability.
- \$10,000.00 Group Life Insurance* - (Following three full months of regular employment*.) This will be augmented with a minimum of \$300,000 life insurance coverage provided as part of an executive bonus plan provided by Equitable Life
- Long Term Disability *- Current policy coverage provided to Aquatech employees
- Short Term Disability- Pending medical documentation after the fourth consecutive day of illness or injury,
Aquatech will provide 100% earnings replacement for first four weeks of consecutive illness and 80% earnings replacement thereafter until the end of week 26.

** Aquatech has filed official request for waiver of waiting period and expects a favorable response from the carrier.*

401 k Retirement Plan:

The Employee will be eligible to participate in the Aquatech 401-K plan at the beginning of the first full pay period in September. Aquatech International Corp. will provide a 25% match (\$0.25 for every \$1.00 that you contribute) up to an employee contribution of 4% of your salary.

Deferred Compensation Plan

Aquatech will contribute 6% of net base salary adjusted annually to a variable life insurance policy offered by Equitable Life and owned by the employee. The employee will designate its own beneficiaries and how monthly premiums paid by the Company will be allocated among various mutual fund categories. This policy provides a substantial life insurance benefit (at least \$300,000). In addition, the employee may receive retirement income from the life insurance policy by keeping the policy in force and accessing cash values through policy loans. The employee can access cash values from the policy after five years.

In the event that the above plan is not desired, Aquatech will provide the option to take payment of a net 6% increase of base salary.

Company Signature and Date:

V.N. James / 8/31/00

Employee Signature and Date:

Karl H. [Signature] 31 Aug 00

Employment Agreement between Aquatech International Corporation and Keith Minnich

Schedule C – Severance

- A. In the event that the Employee's termination of employment by the Company is without cause excluding death or disability, as defined in paragraph 4(a) of the Agreement, the Company shall pay to the Employee, in accordance with the Company's normal payroll practices the equivalent of the Employee's salary for 20 weeks.
- B. In addition, the Company will continue to make the Company's contribution for health insurance for the Employee and his or her eligible dependents during the period of severance listed above, provided that the Employee and his or her eligible dependents elect COBRA continuation coverage.

Company Signature and Date: V. N. Jarama / 8/31/00

Employee Signature and Date: Keith Minnich 31 Aug 00

August 21, 2000

Mark C. Nicholson
N269 W2740 Lelah Avenue
Pewaukee, Wisconsin 53072

Dear Mark:

Aquatech International Corporation is pleased to present to you the following offer of employment and employment agreement, conditioned upon the closing of the Acquisition on or before August 31, 2000. Following are the terms and conditions of your anticipated employment at the close of the Acquisition.

This Employment Agreement (the "Agreement") is by and between Aquatech International Corporation, a Pennsylvania corporation (the "Company" or "Aquatech") and Mark C. Nicholson (the "Employee"). In consideration of the mutual promises set forth, and intending to be legally bound, the Company and the Employee agree as follows:

1. Duties

Employee's title, duties and responsibilities shall be those defined in Schedule A of the Agreement.

2. Compensation

While the Employee remains in the Company's employ, the Company agrees to pay to the Employee, and the Employee agrees to accept, the compensation and benefits listed in Schedule B of the Agreement which is attached and incorporated as part of the Agreement.

3. Term of Agreement

The Agreement shall become effective upon the successful closing of the Acquisition and continue in full force and effect until March 1, 2003.

4. Termination of Employment

a.) The Employee's employment can be terminated by Employee's death, disability or by the Employee's voluntary separation. The Company may terminate the Employee during the term of the Agreement with or without "cause". For purposes of the Agreement the term "cause" shall mean any of the following as determined by the Company in the exercise of good faith and reasonable judgment (i) the willful and continued refusal by the Employee to perform the Employee's duties hereunder, other than by reasons of health, after a written demand for such performance is delivered to the Employee by the Company that identifies the manner in which the Employee has refused to perform the Employee's duties, (ii) the commission of an act by the Employee constituting a felony under state or federal law, (iii) the habitual abuse by the Employee of any substance (such as narcotics or alcohol) which materially affects the Employee's ability to perform the Employee's duties, or (iv) the Employee's engaging in an act of fraud, dishonesty, or gross misconduct in connection with the business of the Company, or (v) conduct by the Employee constituting a material breach of this Agreement. If the Employee terminates his employment for any reason, including death or disability, or if the Employee is terminated for "cause" by the Company, the Employee will not be entitled to receive any compensation or benefits after the effective date of such termination except for life insurance and disability insurance benefits and except as noted in Schedule B - Compensation.

b.) In the event of the Employee's termination of employment by the Company without "cause", the Company shall provide the Employee with severance as outlined in Schedule C of the Agreement (attached).

c.) The Employee acknowledges and agrees that Aquatech's Acquisition of certain assets of Aqua-Chem, Inc.'s water technologies division is motivated to acquire certain processes, know-how and

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information that is critical to the Industrial Concentration and Desalination business (including ZLD applications), of which the Employee has intricate background, knowledge and information. As a result of such background, the Company is willing to provide the Employee with this Agreement in reliance that the Employee will provide such background, knowledge and information regarding the Industrial Concentration business to the Company and its employees during the term of the Agreement. The Employee further acknowledges that if the Employee:

- commits a material breach of the Agreement,
- terminates employment, excluding Employee's death or disability, prior to the expiration of the term of the Agreement, or
- is terminated for "cause" prior to the expiration of the term of the Agreement,

the Employee shall cause the Company to suffer serious and irreparable damage, and therefore, agrees to pay the Company within thirty (30) days of his or her separation any sign-on bonus. He will also forfeit any incentives, accruals unpaid.

5. Confidentiality

- a.) The Employee acknowledges and agrees that certain techniques, manufacturing equipment, and processes have been developed by Aqua-Chem (including Industrial Concentration, ZLD applications, and Desalination business) or by Aquatech which have achieved the status of trade secrets, and that additional trade secrets may be developed during the course of his or her employment; and the Employee agrees not, without approval of the Company, to publish or otherwise disclose or authorize anyone else to publish or disclose either during the term of employment or thereafter, any information, knowledge or data of the Company or its customers, vendors or any other third party with whom the Company conducts business, which the Employee may receive or develop during the course of employment relating to inventions, discoveries, formulas, processes, machines, manufacturers, compositions, computer programs, accounting methods, information systems or business or financial plans or reports, marketing strategies, pricing information, customer lists, prospective customer lists, or other matters which the Employee becomes aware of in the course of employment under this Agreement or heretofore with any company controlled by Aquatech.:

Confidential Information shall not include information that (a) was in the public knowledge at the time of disclosure; (b) was in the knowledge of the receiving party at the time of disclosure; or (c) becomes available to the receiving party on a non-confidential unrestricted basis from a source other than the disclosing party.

- b.) Non-Disclosure of Confidential Information. The Employee agrees that the Employee shall not use, disclose or make available to anyone for use outside the Company's organization at any time, either during the Employee's employment with the Company or subsequent to the termination of the Employee's employment such Confidential Information.

6. Return of Materials

The Employee will at anytime and upon termination for whatever reason immediately return to the Company all Company property without retaining copies.

7. Ownership of Products and Inventions

- a.) The Employee acknowledges and agrees that he shall have no rights of any kind in any products purchased, produced, licensed or sold by the Company (the "Products"). The Employee hereby assigns to the Company any rights in the Products that may be granted the Employee by law (including, without limitation, patent, copyright and trademark laws) or by

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any other person or entity and agrees to execute any documents necessary to transfer any such rights to the Company.

- b.) As one of the conditions to the Employee's employment with the Company and in partial consideration of the payment by the Company to the Employee of such compensation as set out in the Agreement, the Employee agrees that any inventions or improvements capable of use in connection with the business, work, or investigations of the Company, which the Employee may take, invent, acquire or suggest during employment by the Company (whether or not at the request or upon the suggestion of the Company and whether or not during regular hours of work or otherwise during the term of the Employee's employment by the Company) shall become the absolute and exclusive property of the Company. The employee agrees forthwith to assign to the Company full and exclusive rights to any discovery or invention and to any patent to the full end of the term of such patent. The Agreement shall apply to all discoveries or inventions, whether similar to anything used with the present business of the Company or radically different in principal or result. Furthermore, upon the request of the Company, the Employee shall execute all documents necessary or advisable in the opinion of the Company to direct the issuance of patents to the Company or to vest title in the Company to such inventions or discoveries. However, the expense of securing any such patent shall be borne by the Company. Finally, the Employee agrees to hold any secret process, formula, methods, or appliances for which no patent is issued as trustee for the benefit of the Company.

8. Restrictive Covenants

The Employee acknowledges that the Company, at considerable expenditure of time and money, has developed and will develop and provide and/or disclose to the Employee certain Confidential Information as defined in paragraph 5 above and trade secrets. This information is critical to the Company's business and business advantage in providing water and wastewater treatment systems, including Industrial Concentration systems. The Employee further acknowledges that the Company conducts business throughout the United States and internationally.

- a.) The Employee shall not disclose any Confidential Information, directly or indirectly, during the Employee's employment or at any time thereafter, except as required during the performance of the Employee's duties or as required by a court or administrative order.
- b.) The Employee further acknowledges and expressly consents that during the Employee's employment and for twelve (12) months following the termination of the Employee's employment for whatever reason, the Employee, except as required during the performance of the Employee's duties under the provisions of the Agreement shall not, directly or indirectly, in any role or capacity, solicit, assist in the solicitation of or accept any business related to products and services which compete with the Company's products and services from any customer who, during the twelve (12) months prior to the termination of the Employee's employment, had been customers of Aqua-Chem or the Company; or disclose to any person, or business entity of any kind the names or addresses of any such customer; or, directly or indirectly, request, suggest or advise any such to withdraw or cancel any of their business or refuse to continue to do business with the Company. Notwithstanding the above, if the employee's employment is terminated by the Company without cause the applicable length of this non-solicitation provision shall be limited to the length of time that the employee receives severance payments from the Company (Schedule C)
- c.) The Employee expressly consents that during the Employee's employment and for twelve (12) months following the termination of the Employee's employment for whatever reason, the Employee except as required during the performance of the employee's duties under the provisions of the agreement shall not engage, directly or indirectly, in any activities, whether as employer, proprietor, partner, stockholder (other than the holder of less than 1% of the stock of a corporation the securities of which are traded on a national securities exchange or in

18 8/29/00
MAN 8/30/00

the over-the-counter market), director, officer, employee, consultant, agent, principal, or otherwise, in competition with the business of the Company throughout the United States or internationally. Notwithstanding the above, if the employee's employment is terminated by the Company ~~without~~ cause the applicable length of this non-competition provision shall be limited to the length of time that the employee receives severance payments from the Company (Schedule C)

- d.) The Employee expressly consents that during the Employee's employment and for twelve (12) months following the termination of the Employee's employment for whatever reason or for the period of 12 months following the term of the agreement, the Employee, shall not, directly or indirectly, solicit, assist in the solicitation of, hire, or assist in the recruiting of any person employed as an employee or agent of the Company.
- e.) The Employee further acknowledges that in the event of the Employee's termination for any reason, the Employee will be able to earn a livelihood without violating the foregoing restrictive covenants and that the Employee's ability to earn a livelihood without violating such restrictive covenants is a material condition to Employee's acceptance of the Agreement.
- f.) The Employee acknowledges, agrees and expressly consents to submit to equitable injunctive relief if the Employee violates this Paragraph 8 or any other paragraph of the Agreement. This remedy of equitable injunctive relief is in addition to any other remedies at law or equity which the Company may have for breach of the Agreement by the Employee. The Employee acknowledges, agrees and expressly accepts responsibility for any attorney's fees incurred by the Company to enforce or obtain relief under the terms of this paragraph or any other provision of the Agreement or if the Employee loses any associated suit against the Company. The Company agrees to pay legal fees incurred by the Employee in the event there is a breach of agreement by the Company or if the Company loses any associated suit. The Employee agrees that the provisions of this Paragraph 8 are to be effective whether the Employee terminates the employment relationship for any reason or the Company terminates the Employee's employment for cause.

9. No Assignment: Assumption

The Agreement shall be binding upon and inure to the benefit of the successors and assigns of the company. In the event of a future disposition of the Company or including the properties and business of the Company by merger, consolidation, sale of assets, then the Company shall require the acquiring or surviving corporation to assume in writing all of the obligations of the Company hereunder. The Agreement shall inure to the benefit of and be enforceable by the Employee or his legal representatives, executors, heirs or administrators. The Employee may not assign any of his duties, responsibilities, obligations or positions hereunder to any other person.

10. Choice of Law and Forum

The Employee and the Company agree and expressly consent that the Agreement shall be governed by and construed in accordance with the laws of the United States of America and the Commonwealth of Pennsylvania, without regard to principles of conflicts of law.

11. Severability

If any term or provision of the Agreement shall be held to be invalid or unenforceable for any reason, such term or provision shall be ineffective to the extent of such invalidity or unenforceability without invalidating the remaining terms or provisions of the Agreement.

12. Prior Agreements or Modification

VA 8/29/00
MCN 8/30/00

The Agreement supersedes any and all prior agreements, written or oral, between the Employee and the Company concerning the Employee's employment and related matters; No waiver or modification of the Agreement shall be valid unless in writing and duly executed by the parties.

13. Entire Agreement

The Agreement and its attached Schedules A, B and C contains the entire understanding of the parties hereto with respect to the subject matter hereof.

14. Construction

The Agreement will not be construed more strictly against one party than against another party merely by the fact that it may have been prepared by one of the parties, being it recognized that both parties contributed materially and substantially to its preparation.

15. Other Obligations

The Employee represents and warrants to the Company that he is not now under any obligation to any person, firm, corporation, or other entity, and has no interest which is known to be in conflict with his duties and obligations, the terms and conditions of which would prevent, limit, or impair in any way the performance by him of any of the covenants or duties set forth herein.

16. Waivers

No waiver by either party of any breach of nonperformance of any provision or obligation of the Agreement shall be deemed to be a waiver of any preceding or succeeding breach of the same or any other provision of the Agreement.

If you are in agreement with the terms and conditions of the Agreement contained herein, please confirm your agreement in these terms and conditions by executing this Agreement on the line below, at which point the Company and the Employee will be bound by the terms hereto upon the closing of the Acquisition.

Very truly yours,

V. N. Sharma 8/29/00
President

Accepted and agreed to be legally bound,
this 30 day of August, 2000.

[Signature]

Employment Agreement between AquasTech International Corporation and Mark C. Nicholson**Schedule A - Employee's Duties**

Subject to the terms, conditions and provisions of the Agreement, the Company hereby agrees upon the closing of the Acquisition, to employ Mark C. Nicholson as Sr. Process Engineer, or any other comparable position or title as assigned by the Company. Any subsequent changes or modifications to the duties listed below will be made with mutual agreement between Employee and Company.

Duties

The Employee shall devote his knowledge, skill, and his full business time, attention and energies to the performance of services and duties as assigned to him from time to time by or under the authority of the President of the Company or designee including but not limited to:

1. Plans and organizes the assigned activities of an engineering group or section engaged in an engineering program or segment of major project.
2. Estimates resource requirements to provide cost or scheduling information required to meet customer specifications.
3. Initiates or participates in the design or release of new features or products. Insures that available product options are correct and up to date.
4. Communicates technical and/or design information to provide specifications or assistance to customers and other internal departments.
5. Represents the Company as directed in its relationships with customers and/or suppliers
6. Initiates or evaluates new methods or components to enhance products and reduce costs
7. Performs work that generally involves conventional product designs, but may require innovative applications to achieve desired objectives.
8. Provides technical direction to others as required
9. Travel occasionally to participate in technical discussions
10. Remains current on safety regulations as they relate to the product line Communicates these requirements to others as needed
11. May be responsible for the revisions of the technical content of installation and maintenance manuals.

The Employee also shall use his best efforts to promote the interests of the Company.

The Employee shall not accept other employment or permit his personal business interests to interfere with his duties hereunder.

The Company desires that you relocate to the Greater Pittsburgh Metropolitan Area within the next twelve (12) months. Relocation is not mandatory. It is subject to mutual agreement. If this is mutually agreeable between both parties, then the Company will provide support and services to facilitate such relocation to Pittsburgh.

Company Signature and Date:

M. N. James 8/29/00

Employee Signature and Date:

Mark C. Nicholson 30 Aug 2000

Employment Agreement between Aquatech International Corporation and Mark C. Nicholson

Schedule B - Compensation

Salary:

\$72,565.20 per year, payable in accordance with the Company's general salary payment policies. In addition, the employee will receive a sign-on bonus of \$5,500.

Incentive Plan

You will be eligible to participate in the AT/Aqua-Chem IC Incentive Plan. Your target will be 15% of your base salary.

The first 2/3's of your incentive opportunity is based on booked contribution margin and will be paid on a quarterly basis when achieved. 50% of your pay out will be banked, which will then be paid 60 days after the close of the fiscal year. You must be on the payroll on the date the payment is paid.

The remaining 1/3 is based on actual contribution margin, which will be paid 60 days after the close of the fiscal year. You must be on the payroll on the date the payment is paid.

~~In the top line case, the amount of incentive bonus begins with 50% of the bonus paid when the minimum expected contribution margin bookings for the Industrial Concentration profit center has been achieved. The bonus amount will increase in a straight line progression up to 100% of bonus paid when the target contribution margin bookings are achieved. The "expected contribution margin booking" and the "target contribution margin booking" will be mutually agreed and documented. In the bottom line case, the amount of incentive bonus begins with 50% of the bonus paid when the minimum actual contribution margin of the Industrial Concentration profit center has been achieved. The bonus amount will increase in a straight line progression up to 100% of bonus paid when the target actual contribution margin is achieved. Additional bonus will be paid at a greater rate for actual performance beyond the target performance. The "expected actual contribution margin" and the "target actual contribution margin" will be mutually agreed and documented. Targets for bonus measurement in subsequent years (after 2001) will be mutually agreed upon prior to or during the comprehensive performance review of the previous year. A detailed plan will be made available to clearly define plan provisions.~~

In the event of termination without cause, or in the event of death or disability, any earned but unpaid incentive bonus will be paid.

The Employee will be paid any incentive bonus earned during the contract but unpaid if the Employee is on the payroll on the last day of the contract.

Hire Date

The Employee's length of service for determining vacation and 401(K) benefits at the Company is based upon the Employee's hire date at Aqua-Chem. If the Employee separated from Aqua-Chem and was re-hired, then the credited length of service for the start of this Agreement will be the same length of service recognized by Aqua-Chem.

Job Performance Appraisal & Pay Reviews

The current practice at Aquatech International Corp. involves a comprehensive performance review every 12 months with an interim review six months in between. Pay reviews are scheduled in January or July depending upon your start date at AIC.

In your case, you will receive an interim review in January, 2001 and a comprehensive review in June, 2001 with pay review effective July, 2001. During all subsequent years you will receive interim review in the fall (September - October) and comprehensive review in the spring (March - April) with pay reviews effective July 1. This subject to revision based on Company Policy. Aquatech guarantees that base salary of the employee will increase a minimum of 2.5% annually.

Vacation:

The Company agrees to provide the Employee with 13 days paid vacation per year, to be accrued in accordance with the Company's vacation policy. (Vacation allotment will increase to 15 in year 2002.) Three additional vacation days will be available during the calendar year as an adjustment for the difference in paid holidays between Aqua-Chem and Aquatech. Full vacation allotment for year will be made available January 1. Use of vacation days will debit vacation balance and balance will be reflected on payroll stubs. At time of termination of employment, Aquatech will pay on a pro-rated basis any unused vacation days. Prior length of service at Aqua-Chem will be recognized in determining continued vacation accrual after the term of this agreement with no reduction in current allocation.

Vacation days for 2000 will be pro-rated from the effective date of this Agreement until the end of 2000. All three of the additional vacation days provided as an adjustment between paid holidays of Aqua-Chem and Aquatech will be further added onto the pro-rated vacation for 2000.

Benefits:

Benefits for the Employee and his or her dependents, less applicable monthly cost sharing, including, but not limited to, health care insurance, life insurance, retirement plans, and other similar or comparable benefits as may be maintained by the Company from time to time, and made available to the Company's employees. The Company reserves the right to alter, amend or terminate any and all benefit plans and provide Employee with any substitute plans that it may make available to the Company's employees from time to time.

Health Benefits:

The following employer paid benefits will be provided to you and your family:

- Medical Insurance (Blue Card 250) provided at current monthly premium rates in effect for the employees of Aqua-Chem, Inc. Any increases in health insurance cost for the year 2001 and 2002 will be distributed between employer and employee on the same pro-rata basis as the current Blue Card 250 plan.
- Dental Insurance (Comparable)
- Sick Leave - Employee will receive paid sick days for any non-consecutive days of absence due to illness when proper notification (within two hours of start of scheduled work day) is provided to the Employee's supervisor. Consecutive days of illness are subject to provisions under short-term disability.
- \$10,000.00 Group Life Insurance* - This will be augmented with a minimum of \$300,000 life insurance coverage provided as part of an executive bonus plan provided by Equitable Life
- Long Term Disability* - Current policy coverage provided to Aquatech employees
- Short Term Disability - Pending medical documentation after the fourth consecutive day of illness or injury, Aquatech will provide 100% earnings replacement for first four weeks of consecutive illness and 80% earnings replacement thereafter until the end of week 26.

* Aquatech has filed official request for waiver of waiting period and expects a favorable response from the carrier.

401 k Retirement Plan:

The Employee will be eligible to participate in the Aquatech 401-K plan at the beginning of the first full pay period in September. Aquatech International Corp. will provide a 25% match (\$0.25 for every \$1.00 that you contribute) up to an employee contribution of 4% of your salary.

Deferred Compensation Plan

Aquatech will contribute 6% of net base salary adjusted annually to a variable life insurance policy offered by Equitable Life and owned by the employee. The employee will designate its own beneficiaries and how monthly premiums paid by the Company will be allocated among various mutual fund categories. This policy provides a substantial life insurance benefit (at least \$300,000). In addition, the employee may receive retirement income from the life insurance policy by keeping the policy in force and accessing cash values through policy loans. The employee can access cash values from the policy after five years.

In the event that the above plan is not desired, Aquatech will provide the option to take payment of a net 6% increase of base salary.

Company Signature and Date:

V. N. Sharma 8/29/00

Employee Signature and Date:

[Signature] 30 Aug 2000

Employment Agreement between Aquatech International Corporation and Mark C. Nicholson**Schedule C - Severance**

- A. In the event that the Employee's termination of employment by the Company is without cause, excluding death or disability, as defined in paragraph 4(a) of the Agreement, the Company shall pay to the Employee, in accordance with the Company's normal payroll practices, the greater of the following:
1. Employee's salary for the number of weeks that he or she would have received severance under Aqua-Chem's severance policy at the time of the Employee's employment with Aquatech (not to exceed a maximum of \$4,970.00), or
 2. Employee's salary for 12 weeks.
- B. In addition, the Company will continue to make the Company's contribution for health insurance for the Employee and his or her eligible dependents during the period of severance listed above, provided that the Employee and his or her eligible dependents elect COBRA continuation coverage.

Company Signature and Date:

V. N. Sharma 8/29/00

Employee Signature and Date:

Mark C. Nicholson 30 Aug 2000

FedEx US Airbill

Express

FedEx Tracking Number

8600 7215 2886

FedEx ID No.

0215

H32

Sanders Copy

1 From Please print and print hard

Date 03 July 2007 Sender's FedEx Account Number 1029-3758-1
 Sender's Name ROBERT PIETRALA Phone (724) 746-5300

Company AQUATECH INTERNATIONAL CORP

Address 1 FOUR COINS DR

City CANONSBURG

State PA ZIP 15317-1776

2 Your Internal Billing Reference

First 24 characters will appear on invoice.

3 To Recipient's Name DANIELLE HODNICKI Phone (412) 594-5646

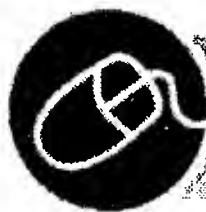
Company TUCKER ARENSBERG

Recipient's Address 1500 ONE PPG PLACE

Address PITTSBURGH

State PA ZIP 15222

0357346756



Ship and track packages at fedex.com
 Simplify your shipping. Manage your account. Access all the tools you need.

4a Express Package Service

☒ FedEx Priority Overnight
 Next business day morning. * Friday shipments will be delivered on Monday unless SATURDAY Delivery is selected.
☐ FedEx Standard Overnight
 Next business day afternoon. * Saturday Delivery NOT available.
☐ FedEx 2Day
 Second business day. ** Thursday shipments will be delivered on Monday unless SATURDAY Delivery is selected.
☐ FedEx Express Saver
 Third business day. * Saturday Delivery NOT available.
 Packages up to 150 lbs.
 FedEx First Overnight
 Earliest next business morning delivery to select locations. * Saturday Delivery NOT available.

4b Express Freight Service

☐ FedEx 1Day Freight*
 Next business day. ** Friday shipments will be delivered on Monday unless SATURDAY Delivery is selected.
☐ FedEx 2Day Freight
 Second business day. ** Thursday shipments will be delivered on Monday unless SATURDAY Delivery is selected.
☐ FedEx 3Day Freight
 Third business day. * Saturday Delivery NOT available.
 Packages over 150 lbs.

5 Packaging

☐ FedEx Envelope*
☒ FedEx Pak*
 Includes FedEx Small Pak, FedEx Large Pak, and FedEx Sturdy Pak.
☐ FedEx Box
☐ FedEx Tube
☐ Other
 * Declared value limit \$500.

6 Special Handling

☐ SATURDAY Delivery
 NOT Available for FedEx Standard Overnight, FedEx First Overnight, FedEx Express Saver, or FedEx 3Day Freight.
☐ HOLD Weekday at FedEx Location
 NOT Available for FedEx First Overnight.
☐ HOLD Saturday at FedEx Location
 Available ONLY for FedEx Priority Overnight and FedEx 1Day to select locations.
 Does this shipment contain dangerous goods?
☐ No ☐ Yes
 Yes: As per attached Shipper's Declaration. Yes: Shipper's Declaration not required.
☐ Dry Ice
 Dry Ice, 5, UN 1845
☐ Cargo Aircraft Only
 Dangerous goods (including dry ice) cannot be shipped in FedEx packaging.

7 Payment Bill to:

☒ Sender
 Sender's FedEx Account No. or Credit Card No. below.
☐ Recipient
☐ Third Party
☐ Credit Card
☐ Cash/Check

FedEx Acct. No.
 Credit Card No.

Total Packages

Total Weight

Total Declared Value¹

\$ 00

¹ Our liability is limited to \$100 unless you declare a higher value. See back for details. By using this Airbill you agree to the service conditions on the back of this Airbill and in the current FedEx Service Guide, including terms that limit our liability. FedEx Use Only

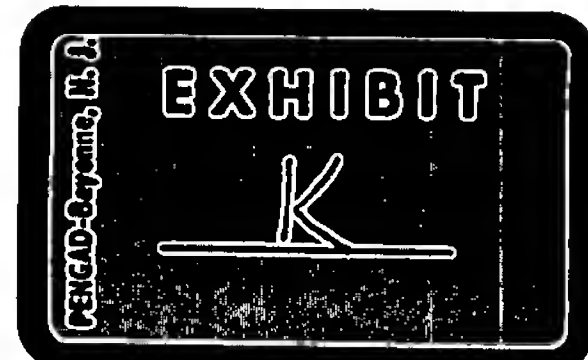
8 NEW Residential Delivery Signature Options

If you require a signature, check Direct or Indirect.

☐ No Signature Required
 Package may be left without obtaining a signature for delivery.
☐ Direct Signature
 Anyone at recipient's address may sign for delivery. This applies.
☒ Indirect Signature
 If no one is available at recipient's address, anyone at a neighboring address may sign for delivery. This applies.

519

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FedEx Billing Online
Express Tracking ID Detail

Tracking ID Summary

Tracking ID Number : 860072152886
Invoice Number : 2-136-50994
Account Number : 1029-3958-1
Invoice Date : 07/09/2007
Due Date : 07/24/2007
Tracking ID Balance Due : \$ 19.75
Invoice Status : Open

FedEx has audited this shipment
Distance Based Pricing, Zone 2
Fuel Surcharge - FedEx has applied

Sender Information

ROBERT PIERALA
AQUATECH INTERNATIONAL CORP

1 FOUR COINS DR
CANONSBURG PA 15317-1778
US

Recipient Information

DANIELLE HODNICKI
TUCKER ARENSBERG
1500 ONE PPG PL

PITTSBURGH , PA 15222
US

Original Reference

Customer Reference# NO REFERENCE INFORMATION
Department#
RMA#
Reference #2
Reference #3

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Updated Reference

Customer Reference#
Department#
Reference #2
Reference #3

Shipment Details

Shipment Date	07/03/2007
Payment Type	Shipper
Service Type	FedEx Priority Overnight
Region Code	02
Package Type	FedEx Box
Pieces	1
Rated Weight	1.0 lbs
Bundle ID	0
Meter No	
Declared Value	0.00

Charges

Transportation Charge	17.40
Fuel Surcharge	2.35
Weekday Delivery	0.00
Total Charges	USD \$ 19.75

Proof of Delivery

Delivery Date	07/05/2007 10:20
Service Area Code	A1
Signed By	D.SANTORO



FedEx Express
Customer Support Trace
3875 Airways Boulevard
Module H, 4th Floor
Memphis, TN 38116

U.S. Mail: PO Box 727
Memphis, TN 38194-4643
Telephone: 901-369-3600

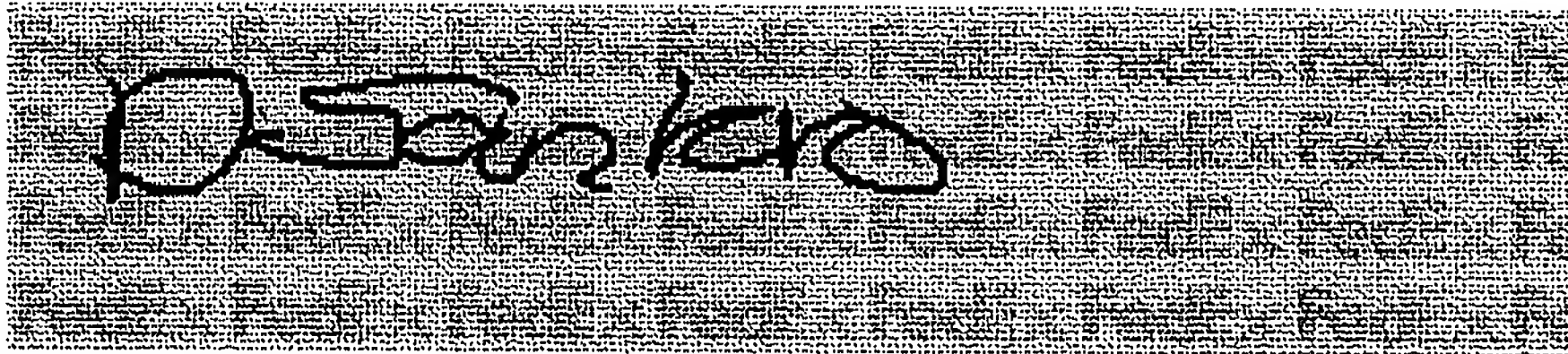
July 17, 2007

Dear Customer:

The following is the proof of delivery you requested with the tracking number **860072152886**.

Delivery Information:

Status:	Delivered	Delivery location:	1 PPG 15 15222
Signed for by:	D.SANTORO	Delivery date:	Jul 5, 2007 10:20
Service type:	Priority Box		



Shipping Information:

Tracking number:	860072152886	Ship date:	Jul 3, 2007
		Weight:	1.0 lbs.

Recipient:
DANIELLE HODNICKI
TUCKER ARENSBERG
1500 ONE PPG PL
15222 US

Shipper:
ROBERT PIERALA
AQUATECH INTERNATIONAL CORP
1 FOUR COINS DR
153171776 US

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